

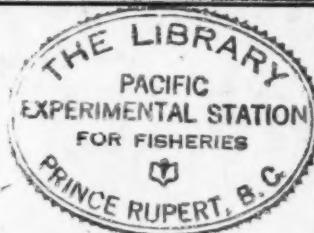
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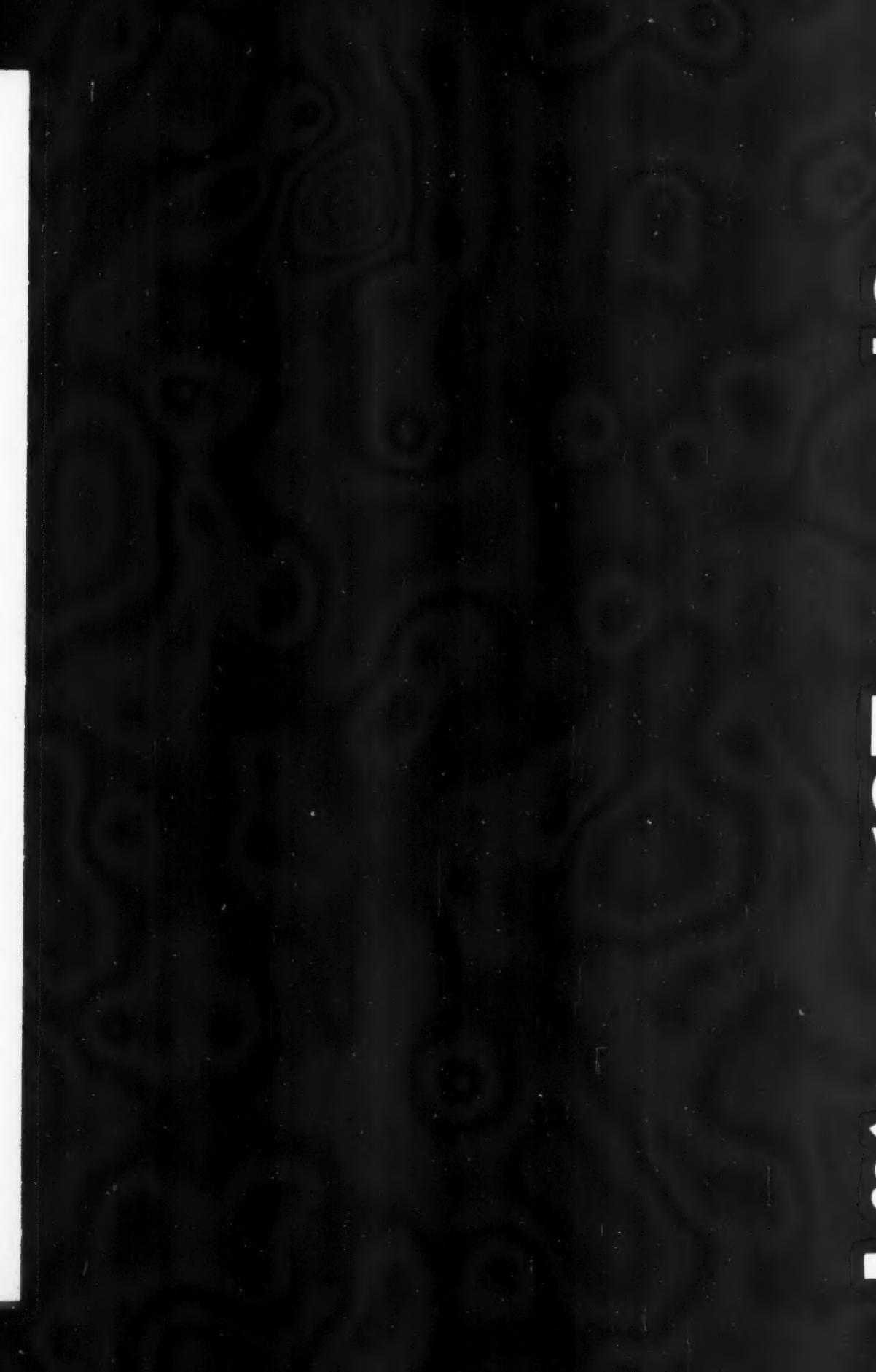
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VOL. 16, SEC. A,

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NUMBER 11

THE SURFACE TENSION OF SOME DILUTE SOLUTIONS¹

By W. C. FISHER² AND C. A. MACKAY³

Abstract

Surface tension measurements have been made on lauric acid at temperatures above its melting point, on aqueous solutions of butyric and lauric acids, and on methyl acetate and sodium oleate. The results for the solutions are compared with those calculated by means of a recent theory.

Introduction

In recent years considerable interest has been shown in surface phenomena, much work having been done both on pure liquids and on solutions. In particular, it has been shown by several workers, whose results are summarized by Bond (3) and Puls (11), that the surface tensions of many pure liquids reach a steady or static value in a very short time, of the order of 0.005 sec., after a fresh surface is formed. It is probable that the initial surface tension exceeds its static value, but the experimental evidence at present is not quite conclusive (4). On the other hand, there is no doubt that the static value of the surface tensions of some solutions is reached only after a much longer period, even amounting to a week according to Adam and Shute (1). Milner (10) has suggested that the change of the surface tensions of solutions depends on the diffusion of the solute into or out of the surface, and that time is required for equilibrium to be reached. Bond and Puls (4) have worked out a mathematical theory based on Milner's hypothesis, from which they have derived an equation for the change of the surface tension of dilute solutions with time, assuming that there is loss of neither solvent nor solute by chemical action or evaporation. Their equation will be considered after the experimental results have been given.

To measure surface tension several methods are available, and a choice must be made of one appropriate to the particular problem. If it is intended to investigate the rate of change of the surface tension with time, the surface should not be disturbed during the period that observations are taken. This requirement is met by a method described by Ferguson and Hakes (6), in which the surface tension is found from the air pressure that is just sufficient to prevent the test liquid from rising in a capillary tube. There are the additional advantages in the method that it is not necessary to have a length

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of capillary tube of uniform bore, which is always difficult to procure, nor is it necessary to measure the contact angle.

Method

Only a brief description of the method will be given here. The tip of a vertical capillary tube is placed at a known depth below the surface of the liquid to be tested. A small air pressure is applied to the meniscus until it is forced to the bottom of the tube, where it is held at the exact level of the tip. The air pressure is read on a suitable manometer. The experiment is repeated with the tip at various convenient depths, such as each centimetre, below the surface. Ferguson and Hakes show that if the pressure corresponding to each position of the tip is read in terms of a difference of height in a manometer, the relation between a given manometer reading h and the surface tension γ is given by the equation

$$dh = d'(h' - r/3) + 2\gamma/gr, \quad (1)$$

where d is the density of the manometer liquid, d' the density of the test liquid, h' the depth of the tip below the surface of the liquid, r the radius of the tip, and g the acceleration of gravity. If a graph is plotted between dh and $(h' - r/3)$ the intercept on the dh axis gives the surface tension when the radius of the tip is known.

Experimental

Distilled water was used in the manometer, which was read with a measuring microscope, giving readings reproducible to within 2.5×10^{-3} cm. The height of the meniscus in the capillary tube was observed through a second microscope mounted close to the first. The liquid to be examined was held in a small glass tube in a thermostat, at a temperature recorded by a copper-constantan thermocouple. The air pressure on the meniscus was regulated by varying the amount of water in a large bottle, which was connected to the capillary tube. A fine control was easily obtained by means of a much smaller vessel in series with the bottle. To reduce variations in temperature, all connecting tubes and vessels were covered with a thick layer of cotton batting. The whole apparatus was set up on rubber stoppers, in a basement room; consequently, jars were reduced to a minimum. After several trials, it was found possible to make a satisfactory glass tip by drawing down a thick walled capillary tube, dipping it in turpentine, and scratching it with a fine file before breaking it off. In this way a clean surface was obtained that was perpendicular to the axis of the tube, with no chips on the inner edge observable under a lower power microscope. The tip had an inner mean diameter of 0.0974 cm.

As a check on the suitability of the apparatus, and the accuracy with which determinations of the surface tension could be made, some preliminary measurements with distilled water were carried out. The manometer was read for five different depths of the tip below the surface of the liquid. To obtain

the best fitting straight line from the experimental data, the method of a residual plot (8, p. 60) was found to be convenient. The result for 25.3° C. was a surface tension of 72.23 dynes per cm. To compare this figure with others, it was reduced to 15° C. and 20° C., the rate of change given in the International Critical Tables being used. At 15° C. the surface tension was found to be 73.76 dynes per cm.; and at 20° C., 73.02 dynes per cm. A few recent determinations are given for comparison; at 15° C. Bond (3) gives 73.83, Ferguson and Hakes (6) 73.54, and Warren (13), as a mean of the results of 13 workers, gives 73.65 dynes per cm. Timmermans and Bodson (12) find the surface tension at 20° C. to be 72.9 dynes per cm. The agreement between these figures and ours suggests that our experimental error is no more than 0.2 dynes per cm., and it may be considerably smaller.

An additional check was available. Two years ago, J. H. Buck made a series of measurements, by the drop weight method, on a 4*N* solution of redistilled butyric acid, over a range of temperatures from 12° to 27° C. Buck's solution was stored in an air-tight glass bottle in a dark closet. His work was repeated, the same solution being used, though no tests were made to determine the concentration, which may have changed slightly in two years. The results are shown in Table I, where our values are marked F. and M.

TABLE I
COMPARISON OF MEASUREMENTS OF SURFACE TENSION (DYNES PER CM.) OF 4*N* BUTYRIC ACID SOLUTION

Temp., °C.	12.8	17.2	21.0	25.1	27.7
Buck	28.68	28.42	28.17	27.92	27.74
F. and M.	28.49	28.17	27.81	27.79	27.49

The mean difference between the surface tensions found by means of the two methods is 0.24 dynes per cm., and the temperature coefficient is almost identical, 0.62 dynes per cm. for each degree.

When the static value of the surface tension of a solution had been found or was already known from other work, a simple procedure, which avoided disturbing the surface, was followed to determine the time rate of change of the surface tension. The tip was placed at a fixed depth, for example, 3 cm. below the surface of the solution. A fresh surface was formed by blowing several air bubbles from the tip; then, as the surface tension varied, the pressure necessary to hold the meniscus at the exact bottom of the capillary tube was read at frequent intervals, timed by means of an electrical stop watch. To obtain the rate of change of the surface tension from these observations, Equation (1) was altered slightly. Let γ_1 and γ_2 be the surface tension at t_1 and t_2 seconds, after a fresh surface is formed. Then since the tip is at a constant depth,

$$\gamma_2 = \gamma_1 - \frac{1}{2}dgr(h_1 - h_2) \quad (2)$$

where h_1 and h_2 are the manometer readings. If γ_1 is the static value of the surface tension, γ_2 may be found from observations of h_1 and h_2 . The method

is useful only to determine rather slow changes in the surface tension, since it requires about 15 sec. to make the necessary readings. The three solutions chosen for experiment were methyl acetate, sodium oleate, and lauric acid in water.

Methyl Acetate

Though the vapor pressure of methyl acetate is so great that the concentration changes appreciably in a few minutes, a series of runs was made with a molar solution. The acetate was supplied by the Eastman Kodak Company. The surface tension increased in 10 min. from 47.0 to 50.5 dynes per cm. at a temperature of 20° C., an increase due in part to a change in concentration. Whether the age of the surface has an effect on the surface tension could not be detected with certainty from the present experiments, owing to the rapid variation in the concentration.

Sodium Oleate

To decrease the rate of change of the surface tension to a convenient value, a concentration of $M/4000$ was used. It was found that in every case the surface tension decreased with the age of the surface, but that successive runs were not reproducible within the limits expected from the results on water and butyric acid, the variations for a given surface age being as great as 3 dynes per cm. Bigelow and Washburn (2) report that they experienced the same difficulty with some of their very dilute solutions. It has been suggested by Harkins and Meyers (9) that this may be due to the entrance into the solution of metallic ions from the glass vessel. Fig. 1, A, shows a typical curve. For a fresh surface the rate of change of the surface tension was so great that no reading could be made until one minute after the meniscus was formed in the capillary tube. The irregularities in the points along the curve are probably due to slight jars or variations in air pressure which disturb the surface. A small intentional change in air pressure caused an increase in the surface tension from 50.2 to 52.8 dynes per cm. Had the observations been continued for an even longer period than that shown in Fig. 1, as was done on one or two occasions, the surface tension would have decreased very slowly until a final static value was reached.

Lauric Acid

Pure lauric acid, melting at 42.6° C., was supplied by the Eastman Kodak Company. Since it seems that very few measurements of the surface tension of pure lauric acid have been made, the surface tension was determined at several temperatures between 44° and 63° C. Table II gives the results.

TABLE II
SURFACE TENSION OF LAURIC ACID, M.P. 42.6° C.

Temp., °C.	44.4	47.5	53.6	63.2
Dynes per cm.	28.63	28.35	27.86	26.96

The acid is nearly insoluble in water; consequently, no attempt was made to measure the concentration of the solutions. Either a saturated solution or the same solution diluted with an equal volume of distilled water was used. The latter concentration is referred to as half-saturated. At temperatures above the melting point of the acid, the surface tension measurements of the solutions were not reproducible with a reasonable experimental error. No

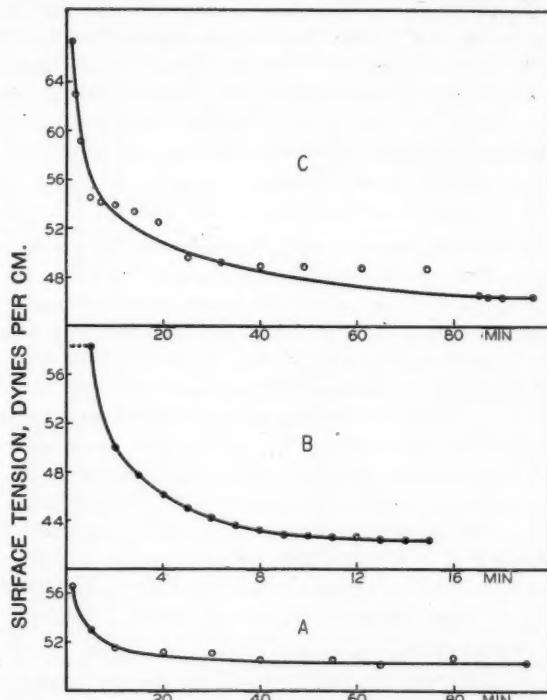


FIG. 1. Decrease of surface tension with the age of the surface of the solution. A. Sodium oleate, M/4000 concentration at 22.1° C. B. Lauric acid solution saturated at 22.2° C. C. Lauric acid solution half-saturated at 25.9° C.

explanation is offered at the present time. No difficulty was experienced in repeating experiments at temperatures below 42° C., and several series of readings were made to determine the static surface tension from 25° to 42° C. Table III gives the results.

TABLE III
STATIC SURFACE TENSION OF A SATURATED SOLUTION OF LAURIC ACID

Temp., °C.	25.3	30.4	39.4	41.5
Dynes per cm.	40.46	37.18	32.05	29.63

Cary and Rideal (5) measured the surface tension of a monomolecular film of lauric acid on water which was slightly acidic. They give a graph which shows that at 25° C. the film has a surface tension of approximately 48 dynes per cm., decreasing 0.73 dynes per cm. for each degree rise in temperature. The corresponding figure from Table III is 0.70 dynes per cm., but the surface tension of the solution was about 7 dynes lower.

Many experiments were made on the variation of the surface tension as the surface aged. Fig. 1, B, shows the mean result at 22.2° C. The separate runs agreed quite well, in contrast to the sodium oleate experiments. It was noticed at once that the surface tension did not change appreciably in the first minute after a new surface was formed, while for sodium oleate the decrease was so rapid during this period that the method of observation was too slow to permit the taking of accurate readings. At higher temperatures, the initial period of constant surface tension was shorter.

The experiments were repeated with the half-saturated solution of lauric acid. The static value of the surface tension was found to be 46.4 dynes per cm. at 25.9° C., while that of the saturated solution was 40.1 dynes per cm. at the same temperature. It also took considerably longer for the surface tension of the more dilute solution to reach the static value. Fig. 1, C, shows a typical curve of the change of the surface tension with the age of the surface at 25.9° C. Whenever a fresh surface was formed by blowing off a few bubbles of air from the capillary tip, the surface tension returned to its initial value and began to decrease at the same rate as before. As was already mentioned, there was a period of inactivity with the saturated solution of lauric acid. The weaker solution may have acted in the same way, but with such a short period that it was not observed. Ferguson and Sharp (7) found that several acids, as well as sodium oleate, had an initial constant surface tension and that at lower temperatures the effect lasted longer.

In the introduction it has been mentioned that Bond and Puls (4) have derived an equation for the relation between the surface tension and the age of the surface of a solution. Their equation for a constant temperature is

$$\frac{(\gamma_0 - \bar{\gamma}) - (\gamma_0 - \gamma)}{\gamma_0 - \bar{\gamma}} = e^{-\frac{2}{\sqrt{\pi}} \sqrt{\frac{t}{T}}}, \quad (3)$$

where γ_0 is the surface tension of water, γ the surface tension t seconds after a new surface is formed, $\bar{\gamma}$ the static surface tension, and T the time for the surface tension to pass halfway to its static value. The equation holds only for dilute solutions, in which the surface concentration is assumed to change by the diffusion of the solute to or from the solution. To compare the theory with experiment the equation may be written

$$\frac{\gamma_0 - \gamma}{\gamma_0 - \bar{\gamma}} = 1 - e^{-\frac{2}{\sqrt{\pi}} \sqrt{\frac{t}{T}}}. \quad (4)$$

A graph of the equation was drawn with t expressed in terms of T as abscissa and $\frac{(\gamma_0 - \gamma)}{(\gamma_0 - \bar{\gamma})}$ as the ordinate. For any given solution, the experimental value of $\frac{(\gamma_0 - \gamma)}{(\gamma_0 - \bar{\gamma})}$ was found for time t . Then T was so chosen that the best fit was obtained between the observed points and the theoretical graph, when t was expressed in terms of T . This has been done in Fig. 2, A, for sodium oleate.

The points show that when T is 2.0 min., the surface tension increases too rapidly at first and too slowly later on. No value of T can be found that would place the experimental points along the graph. Fig. 2, B, shows

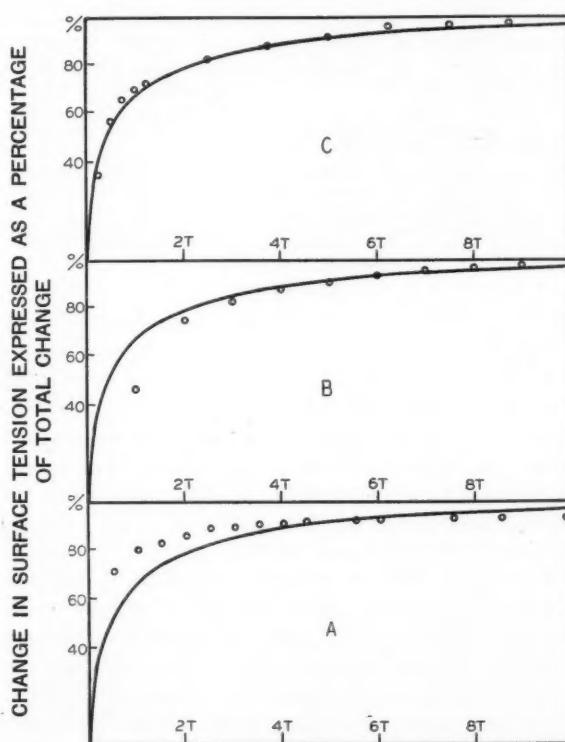


FIG. 2. Comparison between theoretical and experimental rates of decrease of surface tension. A. Sodium oleate solution. $T = 2.0$ min. B. Lauric acid saturated solution. $T = 1.0$ min. C. Lauric acid half-saturated solution. $T = 8.0$ min.

the comparison between theory and experiment for a saturated lauric acid solution, when T is 1.0 min. The initial period of constant surface tension is not accounted for in the theory; consequently, the points fit the theoretical

curve only when t is greater than $2T$. The best agreement between theory and experiment was obtained for a half-saturated lauric acid solution. This is shown in Fig. 2, C, when T is 8.0 min. Too much weight should not be given to these curves, but they do lend some support to the Milner hypothesis. It is hoped to carry on additional work to determine the effect of temperature and inorganic ions on the surface tensions of solutions such as those used in this study.

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DICHLORINE HEXOXIDE¹

BY M. H. KALINA² AND J. W. T. SPINKS³

Abstract

Some chemical and physical properties of dichlorine hexoxide are described and attention is drawn to its dangerous property of exploding violently on contact with organic substances.

The extinction coefficient of solutions of dichlorine hexoxide in carbon tetrachloride solution for a wave-length of 5460 Å has been measured and found to be 2.4, which is very much less than that of liquid dichlorine hexoxide for the same wave-length. A colorimetric method is described for the quantitative estimation of dichlorine hexoxide in solutions. The molecular weight of dichlorine hexoxide in carbon tetrachloride solution has been redetermined, and it confirms the formula Cl_2O_6 .

Solutions of dichlorine hexoxide in carbon tetrachloride are decomposed photochemically by green light. Gaseous chlorine trioxide (ClO_3) is decomposed photochemically by $\lambda 3650$. Its decomposition is photosensitized by chlorine and bromine, the quantum yield in the chlorine sensitized reaction being about 1.

Introduction

Dichlorine hexoxide was first observed in 1843 by Millon (11) who noticed the formation of a red liquid when chlorine dioxide was exposed to sunlight. Dichlorine hexoxide was mentioned again in the literature 80 years later by Bowen (3). In 1925, Bodenstein, Harteck, and Padelt (2) prepared the oxide in a relatively pure state and analyzed it. The analysis indicated that the ratio of chlorine to oxygen was 1 : 3. This fact together with the value for the molecular weight as determined in carbon tetrachloride solution led to the formula Cl_2O_6 . The oxide was therefore named dichlorine hexoxide.

A short time later, while studying the kinetics of the thermal decomposition of ozone sensitized by chlorine, Schumacher and Steiger (14) came to the conclusion that chlorine dioxide and ozone, mixed at ordinary temperatures, should form chlorine trioxide or dichlorine hexoxide. This reaction does, in fact, take place very readily and is the basis of the method commonly used at present. The same method was developed by Allmand and Spinks (1) at about the same time from a study of the photochemical chlorine-ozone reaction.

More recently, the compound has been purified and some of its physical properties measured (6). It has a melting point of $3.5 \pm 0.05^\circ \text{C}$, its color in the liquid state is like that of bromine, and it forms dark orange crystals.

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Canada. From part of a thesis by M. H. Kalina in partial fulfilment of the requirements for the degree of Master of Science.

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on freezing. The crystals are of a light yellow color at -180°C . The density of the liquid is 2.02 gm. per cc. at 3.5°C .

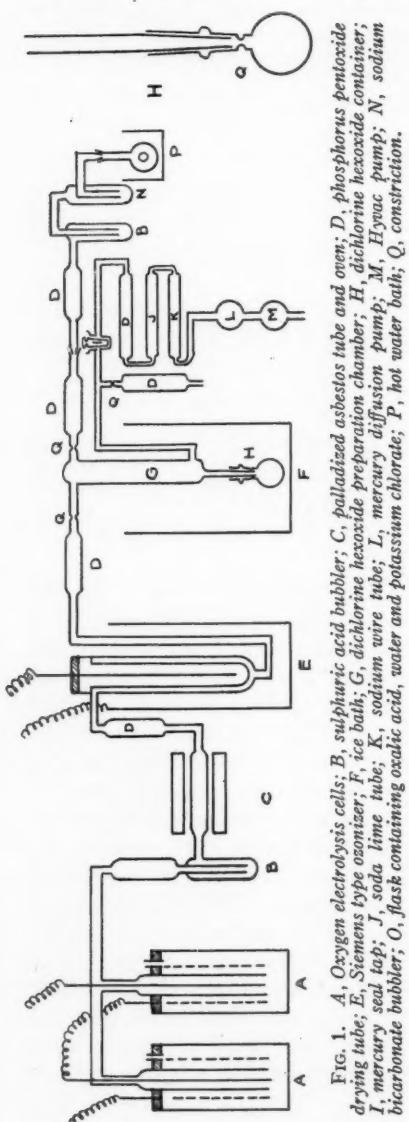


FIG. 1. A, Oxygen electrolysis cells; B, sulfuric acid bubbler; C, palladized asbestos tube and oven; D, phosphorus pentoxide drying tube; E, Siemens type ozonizer; F, ice bath; G, dichlorine hexoxide preparation chamber; H, dichlorine hexoxide container; I, mercury seal tap; J, soda lime tube; K, sodium wire tube; L, mercury diffusion pump; M, Hyvac pump; N, sodium bicarbonate bubbler; O, flask containing oxalic acid, water and potassium chloride; P, hot water bath; Q, constriction.

It is noteworthy that in the gas phase the oxide exists virtually entirely as chlorine trioxide (8). There is a small proportion of chlorine trioxide in the liquid hexoxide also, and the equilibrium, $\text{Cl}_2\text{O}_6 \rightleftharpoons 2\text{ClO}_3$, has been studied by the method of magnetic susceptibilities (4). The equilibrium constant was determined at various temperatures, and from these measurements the energy of dissociation in the liquid state was calculated to be -1730 ± 500 cal.

A short time after the present investigation was started the extinction coefficients of the gas and the liquid were published (7). The long wavelength absorption limit for the liquid hexoxide is at about 6400 \AA , whereas the gaseous trioxide starts absorbing only at about 3600 \AA .

The present work covers (a) experiments on some of the chemical and physical properties of dichlorine hexoxide, (b) the measurement of the extinction coefficient of dichlorine hexoxide in carbon tetrachloride solution, (c) preliminary experiments on the photodecomposition of dichlorine hexoxide and chlorine trioxide.

Preparation of Dichlorine Hexoxide

Essentially, the method of preparation of dichlorine hexoxide consists in mixing dry chlorine dioxide and ozonized oxygen in a suitable glass chamber at about 15°C . (14). The chlorine trioxide produced associates on the walls of the vessel, forming dichlorine hexoxide, which runs to the bottom (Fig. 1), and then into a small collecting bulb immersed in ice. Since dichlorine hexoxide has a great affinity for water, the gases must be thoroughly dried by means of phosphorus pentoxide, and moisture must be rigorously excluded from the apparatus. When it is necessary to transfer the dichlorine hexoxide

on freezing. The crystals are of a light yellow color at -180°C . The density of the liquid is 2.02 gm. per cc. at 3.5°C .

to a special piece of apparatus such as a light-absorption cell, this piece of apparatus is connected to the collecting bulb through a glass septum which can be broken by means of a magnetic hammer.

The chlorine dioxide was prepared by mixing potassium chlorate, oxalic acid, and water in a small container, and heating to 60° C. The gases evolved were passed successively through a saturated sodium bicarbonate solution, concentrated sulphuric acid, and two phosphorus pentoxide tubes.

Ozone was prepared from oxygen in a Siemens type ozonizer operating on 60 cycles and 14,000 volts. The oxygen was prepared by the electrolysis of 20% sodium hydroxide between nickel electrodes. The oxygen was freed from traces of hydrogen, and was thoroughly dried before it passed to the ozonizer.

The dichlorine hexoxide is purified by keeping it at a temperature of 6° C. for about one hour under reduced pressure (Hyvac and mercury pump in series). This removes the more volatile impurities such as chlorine dioxide and leaves a relatively pure product melting at 3.5° C. Dichlorine hexoxide may also be purified by bubbling dry air through it. Another possible method would be to crystallize it from a 2 M solution of dichlorine hexoxide in carbon tetrachloride by cooling to about -23° C. The pure hexoxide crystallizes out in fine bright orange crystals.

Analysis

Thus far, there is no direct analytical method for determining dichlorine hexoxide other than the weighing of the pure substance. When dichlorine hexoxide or its solution in carbon tetrachloride is treated with water, the products of reaction are chlorine dioxide, chloric acid, and perchloric acid. These can be separated and determined by analysis (16); this gives a means of checking the total halogen present. Unfortunately, the ratio of the amounts of these products to the original dichlorine hexoxide is variable; consequently, this method of analysis is not applicable to mixtures of dichlorine hexoxide with the halogens or the halogen oxides. The latter might be formed, for example, by the decomposition of dichlorine hexoxide.

A colorimetric method was therefore developed for the determination of the amount of hexoxide present at any instant in a mixture containing dichlorine hexoxide, chlorine dioxide, and chlorine. It has been found experimentally that solutions of chlorine and chlorine dioxide in carbon tetrachloride do not appreciably absorb the mercury green line at 5460 Å, whereas a solution of dichlorine hexoxide in carbon tetrachloride absorbs 5460 Å strongly. (α_{5460} for chlorine is 0.02; α_{5460} for dichlorine hexoxide is 2.4.) Thus, if the extinction coefficient of dichlorine hexoxide in carbon tetrachloride solution for $\lambda 5460$ is determined by percentage transmission experiments with solutions of known concentration, it should be possible to use percentage transmission measurements of solutions of unknown concentration to determine their concentration. The percentage transmission can be measured either directly by use of a thermopile-galvanometer arrangement, or indirectly

by comparison in a colorimeter with an aqueous solution of potassium dichromate whose percentage transmission is known, monochromatic green light, $\lambda 5460 \text{ \AA}$, being used.

Optical Arrangements

A mercury lamp taking 2 amp. at 140 volts was used as a light source. For accurate work a steady voltage was obtained by means of a voltage regulator*. The light filter for 5460 \AA was a combination of Corning Nonex heat resisting yellow, 2.8 mm. thick; a Corning Didymium glass, 4.97 mm. thick; and a Corning Sextant green filter, 3.97 mm. thick, this serving to cut out the trace of red transmitted by the first two glasses. A Corning red-purple, ultra filter, 3.9 mm. thick, was used for 3650 \AA . The light was measured by means of the usual Moll surface thermopile-galvanometer arrangement. In some experiments a monochromator was used to isolate 5460 \AA from the light of the mercury lamp.

Chemical Properties

Dichlorine hexoxide has a great affinity for water, and it fumes in moist air, the reaction producing mainly chloric acid and perchloric acid. On the addition of the compound to water, dense white fumes are produced, together with some chlorine dioxide (16). When dichlorine hexoxide is added to an alkaline solution or to a solution of potassium iodide in water, there is a violent explosion which usually shatters the beaker. The substance explodes violently on coming into contact with a piece of wood. It also explodes when dropped on to vaseline or brominated grease. When it is spattered into a beaker containing alcohol, there are brilliant flashes and the alcohol ignites. It reacts with graphite and with iodine, but does not explode on coming into contact with them. A solution of dichlorine hexoxide in carbon tetrachloride is immediately decolorized by iodine, iodine tetroxide and iodine pentoxide being formed. No visible reaction takes place with bromine in carbon tetrachloride. Solutions of dichlorine hexoxide in carbon tetrachloride also oxidize sulphur and mercury (10).

When the hexoxide is mixed with sucrose a violent hissing occurs but no explosion—the sugar is presumably dehydrated. In one experiment a small preparation bulb was emptied except for the small amount of dichlorine hexoxide adhering to the walls, and illuminating gas was introduced. A violent explosion resulted, pulverizing the bulb. When bulbs containing liquid dichlorine hexoxide were thrown against a wall no explosion occurred. The vapor was not exploded by a spark from a Tesla coil or from an induction coil.

These experiments indicate that dichlorine hexoxide can give rise to violent explosions, and that particular care should be exercised to avoid contact of dichlorine hexoxide with organic materials. The experimenter should be adequately protected while preparing and handling the liquid hexoxide.

* Suggested by Mr. B. G. Ballard of the National Research Laboratories, Ottawa.

Extinction Coefficient of Dichlorine Hexoxide in Carbon Tetrachloride Solution

Liquid dichlorine hexoxide has a color like that of bromine, and, as already mentioned, its absorption curve has been determined by Goodeve (7). When carbon tetrachloride is added to dichlorine hexoxide the color becomes considerably lighter. Rough experiments with a colorimeter indicated that at 5460 Å the extinction coefficient for the liquid was much greater than that for the carbon tetrachloride solution. It was at first thought that this was due to a dissociation taking place in solution, just as in the gas phase, $\text{Cl}_2\text{O}_6 \rightleftharpoons 2\text{ClO}_3$. However, a repetition of Bodenstein's determinations of the molecular weight in carbon tetrachloride gave a value of 167, very close to the theoretical for dichlorine hexoxide. (In a check on the method, the molecular weight of methyl oxalate was found to be 119; theoretical, 118.)

The first attempt to measure the extinction coefficient of solutions of dichlorine hexoxide in carbon tetrachloride, by matching the solutions in a colorimeter against standard solutions of potassium dichromate, failed. This was due to the introduction of small amounts of moisture, partly with supposedly dry carbon tetrachloride and partly from the air. This moisture could not be entirely excluded.

Consequently, apparatus was built in which dichlorine hexoxide could be dissolved in carbon tetrachloride in the absence of air and moisture (Fig. 2). *A* is a distilling flask containing pure dry carbon tetrachloride (16) and purified phosphorus pentoxide. This is connected to a Gerate glass cell by means of a graded seal *J*. The cell was 1.85 cm. long and 5 cm. in diameter, and had plane ends. After the bulb *A* had been partly filled, this part of the apparatus was evacuated and sealed off at *E*₁. Carbon tetrachloride was distilled back and forth six times from *A* to *B*, and then, after *B* had been filled, the cell was sealed off at *E*₂. The requisite amount of dichlorine hexoxide was made and purified in *D*. After evacuation, this was sealed off at *E*₃. The glass septum was then broken with the magnetic hammer and the dichlorine hexoxide dissolved in the carbon tetrachloride. The cell was then sealed at *E*₄, the free space above the carbon tetrachloride being quite small.

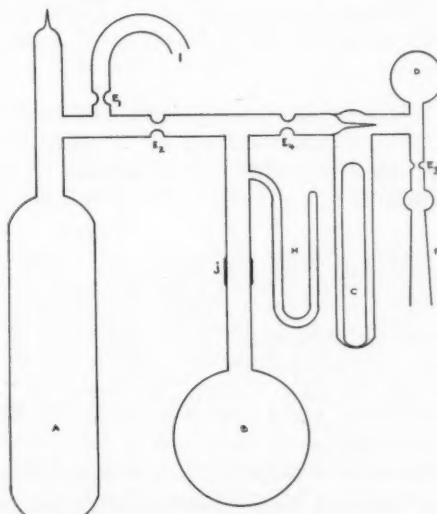


FIG. 2. *A*, distillation flask; *B*, cell; *C*, glass-enclosed hammer; *D*, hexoxide container; *E*, constriction; *F*, ground glass joint; *H*, U-tube for gas removal; *I*, carbon tetrachloride inlet and exhaust tube; *J*, graded glass seal.

The temperature of the dichlorine hexoxide solution was maintained at 3° C. in a thermostat and the percentage transmission measured, the thermopile-galvanometer arrangement and wave-length 5460 Å being used. The molarity of the dichlorine hexoxide could be calculated from a knowledge of the weights of dichlorine hexoxide and carbon tetrachloride used. The weight of dichlorine hexoxide could be checked by analyzing for total halogen at the end of the experiment, the result agreeing well with the weight of dichlorine hexoxide taken.

TABLE I
RESULTS
Length of cell, 1.85 cm.

Molarity	0.0980	0.1075	0.0920	0.0259	0.0570
Per cent transmission	36.1	31.3	41.5	77.2	55.0
Extinction coefficient, α	2.44	2.53	2.24	2.33	2.24

It is seen that the extinction coefficient in carbon tetrachloride solution of molarity of about 0.1 is 2.4. The extinction coefficient for liquid dichlorine hexoxide is 80. In order to account for this difference solely by the dissociation



the dichlorine hexoxide would have to be virtually completely dissociated in solution. Molecular weight measurements indicate that in solution the hexoxide certainly does not dissociate to this extent. One might perhaps argue that the molecular weight measurements were made at -27° C., whereas the light absorption measurements were made at 3° C., and that the equilibrium might have been shifted by the temperature. However, such an explanation seems quite out of the question, as it would require a heat of dissociation of dichlorine hexoxide in solution of about 36,000 calories. (The corresponding heat of dissociation in the liquid phase is 1700 calories.)

The failure of the above chemical explanation leads to the suggestion that the difference between the extinction coefficients in the pure liquid and in carbon tetrachloride solution is due to a difference between the actual absorption of light by the molecules in solution and the absorption by molecules in the pure liquid state. This difference might be attributable either to (a) extensive solvation in carbon tetrachloride solution, or (b) to the fact that in the pure liquid the molecules are subject to strong fields which increase the transition probability between the normal and an excited state of the molecule, and thereby lead to an increase in the extinction coefficient. In view of the normal molecular weight in solution, this last explanation is favored.

While examples of a change in extinction coefficient due to a highly polar solvent, or compound formation, or hydration of ions are fairly common in the literature, only one other change similar to that observed in this work was found; namely, the change in the extinction coefficient of pure liquid bromine

when it is dissolved in an inert solvent (12). The absorption of light by bromine in the gaseous and liquid states and in solution has been investigated. The absorption curves show that for some wave-lengths the extinction coefficients in the three states are not very different. However, at 3080 Å, the extinction coefficients for liquid, solution, and gas are 630, 14.5, and 1.12, respectively. This is quite comparable to the effect with dichlorine hexoxide. The explanation given for the change in the extinction coefficient of bromine is that part of the absorption at 3080 Å is due to an intercombination transition $^1\Sigma - {}^3\Pi$. Electric fields favor the occurrence of such intercombinations, and it is suggested that the field of the surrounding molecules increases the probability of such a transition, thereby increasing the extinction coefficient. The effect is apparently stronger in pure liquid bromine than in a solution in carbon tetrachloride, where the bromine molecules are relatively far apart. A similar explanation might very well apply to the change in the coefficient of dichlorine hexoxide. However, thus far nothing is known of the potential curves for dichlorine hexoxide.

Measurements of extinction coefficients in the vapor phase and in solution for a given substance are rather more plentiful. Chlorine, for example, at 3300 Å, has a higher extinction coefficient in solution than in the gas phase (5, 9), whereas the extinction coefficients of iodine in the two phases are quite similar.

While the data are not sufficiently extensive to permit a detailed analysis, it does appear that in the transition from a gaseous phase to a solution, the validity of Beer's law is the exception rather than the rule (13). In this transition and in that from liquid to solution, a change in extinction coefficient might reasonably be expected if the two species of molecules did not have identical external fields. It is supposed for the moment, of course, that the solvent is inert and non-polar.

Photodecomposition of Dichlorine Hexoxide in Carbon Tetrachloride Solution

The extinction coefficient of dichlorine hexoxide at 5460 Å having been determined, it is obviously possible to follow changes in concentration by measuring the percentage transmission of 5460 Å from time to time. In this way, it is found that a 0.1 *M* solution of dichlorine hexoxide in carbon tetrachloride decomposes thermally quite rapidly at 2° C. The reaction is accelerated by green light, and rough measurements indicate a quantum yield of about 10 under our conditions.

Photodecomposition of Chlorine Trioxide in the Gaseous Phase

As we have already mentioned, dichlorine hexoxide exists mainly as chlorine trioxide in the gaseous phase, and it begins to absorb light strongly only at 3600 Å. Preliminary experiments in the photodecomposition have been carried out with the apparatus illustrated in Fig. 3. The over-all equation for the total decomposition of chlorine trioxide is $2\text{ClO}_3 \rightarrow \text{Cl}_2 + 3\text{O}_2$. Consequently, in a constant volume system, the reaction can be followed by

the change in pressure. This was measured by means of a calibrated glass spoon gauge. The tip of the pointer attached to the gauge moved 0.709 mm. for a change in pressure of 1 mm. of mercury. The dichlorine hexoxide was made in a small bulb as described previously and sealed on to the apparatus at *A*. *B* is an outlet tube enabling this to be done. *B* was then sealed off and the pressure in the cell and both sides of the gauge was reduced to a very low value by means of a mercury pump. The outside of the gauge was isolated by closing tap *H*. The septum *D* was then broken and dichlorine hexoxide pumped through the apparatus, after which constrictions *I* and *C* were sealed off, in the order mentioned. The cell was then illuminated and the reaction followed by the change of pressure shown by the spoon gauge.

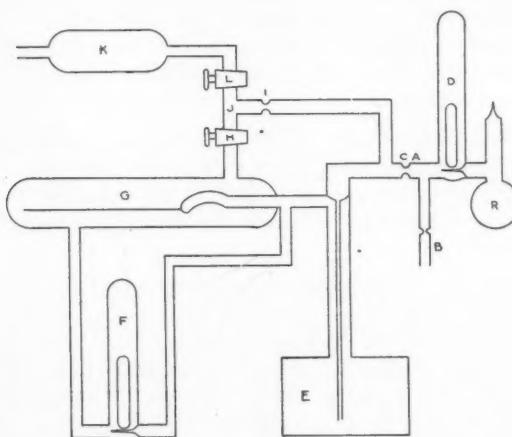


FIG. 3. *A*, straight line seal; *B*, side tube and constriction; *C* and *I*, constrictions; *D* and *F*, hammers and septa; *E*, cell; *G*, spoon gauge; *H* and *L*, taps; *K*, sodium wire tube; *R*, dichlorine hexoxide container.

Preliminary experiments indicate that chlorine trioxide is relatively stable thermally (as compared to dichlorine hexoxide in solution) at 15° C., and is photodecomposed by 3650 Å.

Chlorine trioxide also undergoes a chlorine sensitized decomposition at 3650 Å, the quantum yield being approximately unity. (Details of these experiments will be found in Reference (10).)

A bromine sensitized decomposition of chlorine trioxide has also been reported in the literature (15).

Since an exact investigation of the photokinetics of these reactions is obviously beset with considerable difficulties, it is being postponed until a more detailed study of the chemical and thermochemical properties of dichlorine hexoxide has been made.

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THE EFFECT OF POLYHYDRIC ALCOHOLS ON THE TIME OF SET OF ALKALINE SILICA GELS¹

By L. A. MUNRO² AND J. A. PEARCE³

Abstract

The behavior of glycerol in increasing the time of set of alkaline silica gels is not anomalous. There is a regular and further increase in time of set when the higher members of a series of polyhydric alcohols are added to the gels. The rate of change in the effect produced by increasing concentration of the addition agent varies with the concentration and pH. With the 2.23% gel, at pH 8.2, glycol showed a reversal of its effect on the time of set. The implications of this change are discussed.

In a previous study (4) on the effect of addition agents on the time of set of alkaline silica gels it was noted that glycerol showed anomalous behavior. Instead of the regular decrease in time of set caused by increasing amounts of the homologous series of soluble aliphatic alcohols, a marked increase in the setting time was caused by glycerol. Furthermore, although glycol decreased the time of set, the effect was much less than that obtained with the monohydric alcohols. It seemed of interest to extend the investigation to higher polyhydric alcohols. These have been studied over a range of pH and at two concentrations of silica.

Experimental

The silicate used was Baker's best grade of "Crystalline Sodium Silicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ". Analysis of this gave the molar ratio of Na_2O to SiO_2 as 1.00 : 1.02. The water employed for making up solutions was redistilled and boiled before use. The stock sodium silicate solution was made up to a solution of specific gravity of 1.1569 (Westphal balance) in 1.5 to 2 litre batches. Larger volumes were avoided because it was observed that on prolonged standing a precipitate gradually formed. This aged silicate gave a slightly longer time of set (e.g., from 210 to 225 sec.). The silicate solution was found to contain 6.7% of SiO_2 . The solution was kept in a waxed Pyrex flask, as coatings of collodion, vaseline, and bakelite varnish had proved to be unsatisfactory.

The acetic acid was prepared by diluting 50 cc. of glacial acetic with 500 cc. of water. The addition agents were Eastman's best grade.

The time of set was determined by the tilted rod method of Hurd and Letteron (2).

The procedure of mixing was the same as that previously described (4). The liquids were added in 1.0, 2.0, and 3.0 cc. portions to the acid and made up to 25 cc. with water. The solids were added to the acid in 0.5, 2.0, and 4.0 gm. portions, and the whole was made up to volume.

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The total weight of the largest amount of the difficultly soluble mannitol was added in a blank experiment to the mixed acid and silicate. This gave the volume of water necessary to bring the final volume to 50 cc. In the determination of the time of set for this particular addition agent the total quantity of agent was added to the acid plus the determined amount of water, and the silicate was then added, with rapid stirring. Complete and rapid solution was obtained.

Hurd, Raymond, and Miller (3) observed in their experiments a rise of 1.5°C . due to heat of neutralization. The present authors noted that with rapid-setting gels and high concentrations of addition substances there was a rise in temperature of four degrees on the addition of the silicate to the acid and addition agent. If the reagents were cooled and mixed in the beaker in a $16.0 \pm 0.1^{\circ}\text{C}$. thermostat the temperature rose in a few seconds to 20° ; at this point the beaker was transferred to a $20.00 \pm 0.01^{\circ}\text{C}$. thermostat where setting proceeded at this temperature.

Owing to the slight solubility of dulcitol, with accompanying experimental difficulties, only one run was made. However, it appears that this alcohol is similar to mannitol in its effect.

Results*

The results are shown graphically in Figs. 1 to 5. In Figs. 1 to 4 the time of set is plotted against the molar concentration of addition agent. Fig. 5 shows the induced change in setting time as percentage of the original time

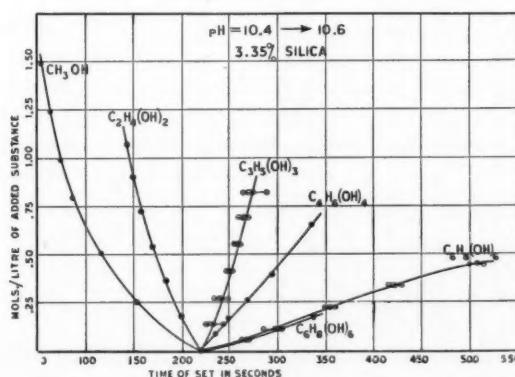


FIG. 1. Silica gels, pH 10.4-10.6; prepared by adding 25 cc. Na_2SiO_4 solution (3.35% SiO_2) to 25 cc. acid mixture (16 cc. dilute acetic + addition agent + water). Curve 5— $\text{C}_6\text{H}_{13}(\text{OH})_6$, mannitol. Curve 6— $\text{C}_6\text{H}_{13}(\text{OH})_6$, dulcitol.

of set for different molar concentrations of added substance. These curves are the mean of several determinations made at different times, with different batches of silicate and addition agents. The greatest variation observed

* Since the data are shown graphically, the tables of data have been omitted.

in the setting time of a gel of pH 10.4 was ± 7 sec. Curves 3 and 5, Fig. 1, show the typical relation of the curves to the divergent values. In no case is there any doubt as to the order in which the addition agents affect the time of set.

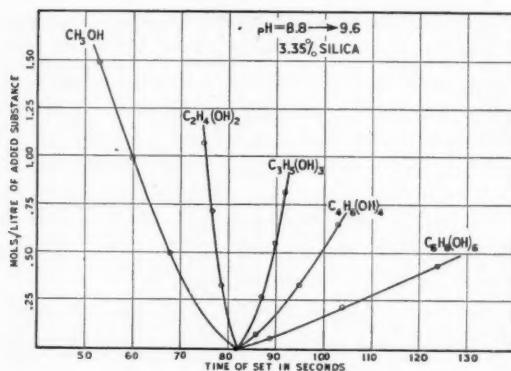


FIG. 2. Silica gels, pH 8.8-9.6; 25 cc. Na_2SiO_3 solution (3.35% SiO_2) + 25 cc. acid mixture (18.5 cc. dilute acid + addition agent + water).

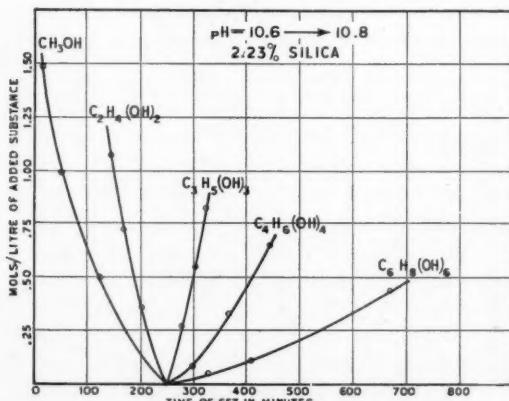


FIG. 3. Silica gels, pH 10.6-10.8; 25 cc. Na_2SiO_3 solution (2.23% SiO_2) + 25 cc. acid mixture (10 cc. dilute acid + addition agent + water).

As was noted previously, the pH, observed colorimetrically, increased on setting of the gel and with increased amounts of addition agents. With methanol the shift is greater; with glycol it is less; while with glycerol, erythritol, and mannitol the pH was the same as that of the original gel. In the case of methyl alcohol, for instance, 3 cc. of the addition agent gives a gel of pH 10.6, changing to 10.9, whereas the pH of the original gel without addition agent is initially

10.4, increasing to 10.6. The addition of 4 gm. of mannitol gave a pH of 10.4 to 10.6. The graphs, with the exception of No. 5, show a change in pH of the original gel on setting. In Fig. 5 the pH given represents the initial pH of the original gel.

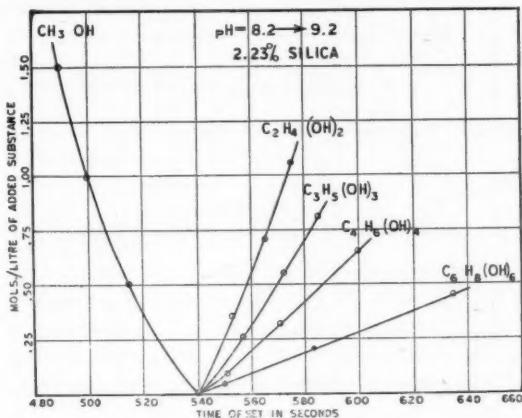


FIG. 4. Silica gels, pH 8.2-9.2; 25 cc. Na_2SiO_4 solution (2.23% SiO_2) + 25 cc. acid mixture (12.5 cc. dilute acid + addition agent + water).

Discussion

These experiments show conclusively that the previously observed behavior of glycerol is not anomalous, but is a regular step that progresses as the number of $>\text{CHOH}$ groups increases (Figs. 1 to 4). The lengthening of the time of set of glycerol gels increases with the pH. This is in sharp contrast to the rapidly decreasing time of set with increasing pH for gels containing the monohydric alcohols such as methanol.

When the results are expressed as percentage change in time of set, a series of curves is obtained for each addition agent. It will be seen that slope changes with pH and concentration. Further it may be noted that the change in slope with change in pH is more pronounced with the gels of lower concentration. The effect of concentration and pH on the slope of the curves is most pronounced with the members at the extremes of the series, *viz.*, methanol and mannitol.

It will be observed that the curve obtained with glycol and the dilute gel at pH of 8.2 shows a reversal of slope (Figs. 4 and 5). This addition agent now behaves as glycerol, *i.e.*, it increases the time of set. Since it is known that the effect of an addition agent on acid gels is opposite to that on alkaline gels (6), one would expect a definite pH at which this reversal takes place—at first thought, the isoelectric point of silica sol, the pH of minimum set, which has been stated by Prasad and Hattiangadi (5) to be 7.6. The fact

that the glycol effect changes between pH 8.2 and 10.6 indicates that this is not the case.

The pH at which the alcohols change from retarding to accelerating agents probably varies with the addition agent. Coehn (1) states that differences in the dielectric constants of the addition agents cause differences in charge

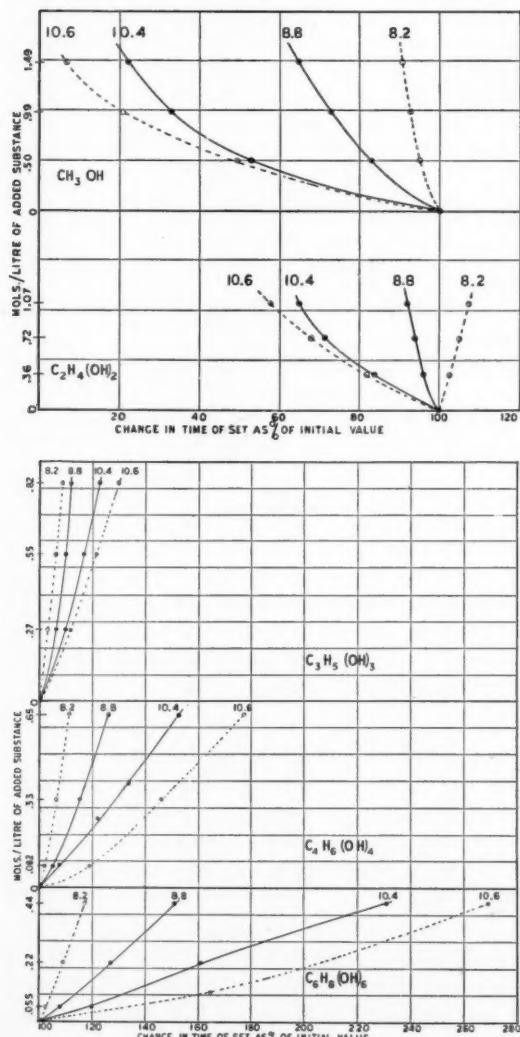


FIG. 5. Solid curves—gels from "3.35%" silicate, pH 8.8 and 10.4; broken curves—gels from "2.23%" silicate, pH 8.2 and 10.6.

on the colloidal particle. This implies a specific effect on the stability of the silica sol with consequent influence on the time of set. Differences in the concentration of the gel and its attendant electrolytes play important roles. Other factors will also be operative.

It is proposed to investigate this shift in behavior in relation to the pH of the gels of minimum setting time, the concentration of silica, and the dielectric constants of the addition agents.

Acknowledgment

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EQUILIBRIA IN TWO-PHASE, GAS-LIQUID HYDROCARBON SYSTEMS

IV. METHANE AND HEPTANE¹

By E. H. BOOMER², C. A. JOHNSON³, AND A. G. A. PIERCEY⁴

Abstract

The densities and compositions of both phases in the methane-*n*-heptane solubility equilibrium have been determined at 25°, 55°, and 85° C. at total pressures from 35 to 250 atm. The critical pressures of complete miscibility were found, and the properties of the system are discussed. The nitrogen-*n*-heptane system was investigated similarly at 100.9 atm. and temperatures from 25° to 115° C. The system composed of Viking natural gas and impure heptanes was also investigated at 25° C. The three systems, methane-pentane, -hexane, and -heptane are compared and discussed.

Introduction

In previous investigations (2, 3) the methane-pentane and methane-hexane systems have been examined. The properties of both phases in equilibrium were determined at three temperatures and pressures up to the point of complete miscibility. In the present paper are presented the results obtained with the system *n*-heptane-methane, together with measurements on a system composed of *n*-heptane and a gas that is virtually pure methane, and those on the system *n*-heptane-nitrogen. The last-mentioned measurements were made in an effort to determine the effect of 5.6% of nitrogen in the gas used generally in this work. It may be said that the effect of the nitrogen is barely noticeable. In addition some measurements, preliminary to those outlined above, were made with impure heptane and a dry, high-methane natural gas from the Viking field.

This paper completes the publication of a series of measurements in which the normal paraffin hydrocarbons, pentane, hexane, and heptane have been used; it will be followed by reports on systems composed of naphthenic and aromatic hydrocarbons. In view of this, it is felt that the present paper should include a review of the three paraffin systems investigated, and discuss the relation between them. Consequently some of the data reported previously (2, 3) will appear again in this paper in one table and in one figure.

Materials

The gas used in the principal measurements has been described in previous reports (3). It had the composition: methane, 94.4; nitrogen 5.6%. Natural gas from the Viking field, Alberta, was also used in preliminary work on the

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heptane system. This gas was taken from the supply mains, scrubbed with concentrated sulphuric acid to decompose odorant sulphur compounds added to the gas, and then passed over solid potassium hydroxide. The gas was dry and had the following composition on conventional analysis and combustion by means of the Orsat apparatus (Burrell): methane, 90.8; ethane, 3.5; nitrogen, 5.7%; density (N.T.P.), 0.000773 gm. per cc.

The gas contained some propane, possibly 1%, and traces of butane. The pressure-volume-density relations of this gas at 25° C. are given in Table I.

TABLE I
PRESSURE-VOLUME-DENSITY RELATIONS OF VIKING NATURAL GAS AT 25° C.
Methane, 90.8; ethane, 3.5; nitrogen, 5.7%

Pressure, atm.	Density, gm. per cc.	Deviation PV/P_1V_1	Pressure, atm.	Density, gm. per cc.	Deviation PV/P_1V_1
1	0.0007085	1.0	202.7	0.1730	0.8302
36.7	0.02727	0.9535	237.2	0.1969	0.8534
68.9	0.05446	0.8963	245.4	0.2021	0.8602
102.3	0.08504	0.8522	277.4	0.2193	0.8963
134.8	0.1164	0.8218	312.6	0.2358	0.9390
168.7	0.1458	0.8196			

The gas is slightly less ideal than the other gas used, as might be expected from its content of higher hydrocarbons.

In order to determine the influence of the nitrogen in the above-mentioned gases on the results, a third gas, virtually pure methane, was prepared. Viking natural gas was liquefied at atmospheric pressure by means of liquid air. The condenser was fitted with a small electric heater and a short, wire-packed distilling column. The condensed natural gas was distilled through this column. The composition of the overhead gas was followed continuously by means of a thermal conductivity, gas analysis apparatus. While nitrogen was distilling, the gas was vented to the atmosphere. The methane fraction was collected in gas-holders and compressed in storage cylinders. The residue, ethane, propane, water, etc., were discarded. A single run required 3.5 hr. and yielded about 60 litres of gas. It was not found possible to prepare pure methane with the apparatus. The gas produced always contained some nitrogen, from 0.3 to 0.5%, as impurity.

In the experiments with pure nitrogen, the commercial product supplied in steel cylinders under pressure was used. It was freed from oxygen by passage over hot copper, and dried under pressure.

Three different liquids were used in this work. Material of boiling range 90 to 95° C. was obtained by the fractional distillation of a light petroleum distillate. This material was nitrated thoroughly, washed, and dried. It was then distilled through a 38 in. vacuum-jacketed, packed column, and the fraction boiling over the range 90 to 93° C. (679 mm. of mercury) was retained. The density of the product was 0.704 at 20° C., this high value suggesting the presence of cycloparaffins.

An attempt was made to obtain *n*-heptane from Turner Valley naphtha. The 80 to 100° C. fraction was washed with sulphuric acid until no discoloration was observed. This material was washed, dried, and fractionated. The 75° to 94° C. fraction was nitrated thoroughly and then sulphonated by refluxing with fuming sulphuric acid for 48 hr. The 83 to 95° C. fraction was retained. The density, 0.707, and refractive index, 1.3961, at 21° C. indicated the presence of cycloparaffins.

Jeffery Pine Oil was the source of the *n*-heptane. This *n*-heptane was carefully distilled with high reflux through the column mentioned above. The physical constants of the middle portion remained unchanged on fractionation and this portion was used as *n*-heptane. The properties were: density, 20° C., 0.6834 (0.684, I.C.T.); refractive index, 22.5° C., 1.3863 (1.3867, I.C.T.).

Results and Discussion

The results and comparisons with other systems are presented in Tables II to VII inclusive, and in Figs. 1 to 7. The symbols have the same significance as those used previously (2, 3). Single primes refer to the gas phase, double primes to the liquid phase; the subscript 1 refers to the gas, usually methane, and subscript 2 refers to the liquid, heptane. The mole has been used to express quantities except in the results obtained with the impure heptanes and Viking gas; in these the mass fraction is used.

TABLE II
VIKING-NATURAL-GAS-IMPURE-HEPTANES SOLUBILITY
EQUILIBRIA AT 25° C.

Pressure, atm.	Phase density, gm. per cc.		Phase composition, weight % heptane	
	Liquid	Gas	Liquid	Gas
<i>Heptane from petroleum</i>				
136.8	0.6045	0.1265	86.1	6.6
172.4	0.561	0.172	80.0	11.5
204.6	0.517	0.223	73.4	19.0
237.9	0.440	0.309	61.1	36.3
238.1	0.444	0.311	61.0	36.5
<i>Heptane from Turner Valley naphtha</i>				
237.9	0.457	0.301	62.5	32.8

changes in vapor content of the gas phase.

As a general rule, the mutual solubility of gas and liquid pairs will increase as the gas and liquid become more nearly alike in physical and chemical properties. The *n*-heptane-ethane system, investigated by Kay (5), shows

Impure Heptanes

The data obtained in experiments with impure heptanes and Viking gas are shown in Table II. These results are shown graphically in Fig. 1 together with the corresponding data for the *n*-heptane-methane (5.6% of nitrogen) system. Compositions are expressed in weight per cent because of uncertainty as to the nature of the impure heptanes. It is interesting to compare Fig. 1 (weight per cent ordinate) with Fig. 3 (mole per cent ordinate). The curves in the former are very useful in magnifying the

greater mutual solubility and a much lower pressure of complete miscibility than were found in the present work with gases consisting substantially of methane. Hence, it might be predicted that Viking gas, in virtue of its content of higher gaseous hydrocarbons, would be more soluble than methane containing 5.6% of nitrogen in the same liquid hydrocarbon. Reference to Fig. 1 shows that this is the case.

It is probable that the nature of the liquids used with Viking gas accounts in part for the results. Both impure heptanes are mixtures containing branch chain, and straight chain, paraffin hydrocarbons and possibly cycloparaffins in small amounts. The influence of the branch chain paraffins will be predominant and this influence, compared with that of the straight chain, *n*-heptane, will be one of increased mutual solubility between gas and liquid.

Thus, the differences between the results with the impure-heptanes-Viking-gas systems and the *n*-heptane-methane (5.6% of nitrogen) system are in the direction expected, and may be accounted for by both the composition of the impure heptanes and the composition of Viking gas.

Normal-heptane-Methane (5.6% of Nitrogen)

The data for the *n*-heptane-methane system are given in Table III, and the properties of the system are illustrated in Fig. 2, showing phase density, in Fig. 3 showing phase composition, in Fig. 4 showing solubilities as mole ratios, and in Fig. 5 showing the equilibrium constants for methane and *n*-heptane. Because of the great variation of the equilibrium constants in this system, the constants have been plotted on a semilogarithmic graph. The general shape of the curves is not altered greatly by this procedure. The properties of the system at the pressure of complete miscibility for each temperature, together with the same data for the systems pentane- and hexane-methane are given in Table VII.

This system behaves in all respects much as expected in the light of previous results with pentane (3) and hexane (2). The lower volatility and higher molecular weight of *n*-heptane may be used to give a qualitative account of the differences between the three systems.

The *n*-heptane system obeys Henry's law with reasonable accuracy up to pressures of almost 100 atm. Deviations are appreciable at lower pressures but become marked only at higher pressures. The liquid composition curves,

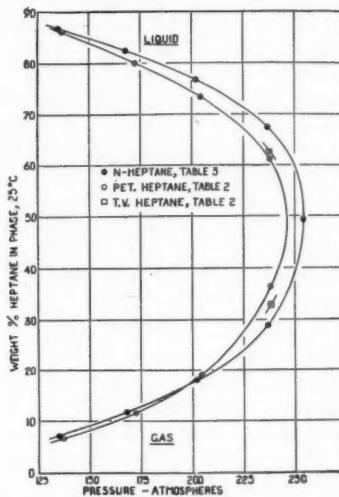


FIG. 1. Composition in weight per cent of gas and liquid phases at 25°C as a function of pressure for *n*-heptane-methane (5.6% of nitrogen) and impure-heptanes-Viking-gas systems.

TABLE III
METHANE (5.6% N₂)-*n*-HEPTANE SOLUBILITY EQUILIBRIUM

Pressure, atm.	Phase density, gm. per cc.		Phase composition, mole %						Solubility	Equilibrium constant		
			Liquid			Gas						
	Liquid	Gas	C ₇ H ₁₆	CH ₄	N ₂	C ₇ H ₁₆	CH ₄	N ₂				

Temperature, 25° C.

1	0.679					4.5	94.5				
36.2	0.661	0.0298	83.5	16.3	0.2	1.75	92.85	5.4	0.192	0.0178	0.0209
	0.659	0.0280	83.8	15.9	0.3	—	—	—			
68.4	0.637	0.0538	71.6	27.6	0.8	1.01	93.2	5.79	0.385	0.0116	0.0161
	0.634	0.0554	—	—	—	1.29	92.8	5.91			
101.7	0.610	0.0873	61.5	37.6	0.9	1.09	92.5	6.41	0.624	0.0110	0.0178
	0.610	0.0859	60.8	38.7	0.5	1.09	93.6	5.31			
135	0.585	0.122	51.8	47.0	1.2	1.33	90.8	7.87	0.907	0.0128	0.0244
	0.584	0.121	—	—	—	1.19	91.0	7.81			
167.9	0.556	0.161	43.5	53.9	2.6	2.20	91.0	6.8	1.235	0.0222	0.0498
	0.555	0.160	43.8	54.0	2.2	2.15	91.0	6.85			
202.2	0.521	0.208	35.4	62.2	2.4	3.7	89.4	6.9	1.752	0.0373	0.1017
	0.521	0.206	35.4	61.9	2.7	3.5	89.9	6.6			
236.0	0.466	0.267	26.0	70.5	3.5	—	—	—	2.71	0.0684	0.251
	0.457	0.269	25.5	70.5	4.0	6.4	87.1	6.5			
243.6	0.444	0.293	22.6	73.1	4.3	8.3	85.8	7.9	3.23	0.0905	0.367
	0.414	0.324	19.2	76.1	4.7	9.6	84.9	5.5			
253.3	0.395	0.390	—	—	—	—	—	—	—	0.106	0.500

Temperature, 55° C.

1	0.653					23.1	76.9				
34.8	0.628	0.0267				3.2	90.4	6.4	0.165	0.0331	0.0374
	0.634	0.0254	85.5	14.1	0.4	—	—	—			
100.9	0.594	0.0765	63.9	35.2	0.9	2.1	92.8	5.1	0.551	0.0215	0.0329
	0.540	0.141	46.8	51.3	1.9	3.2	90.6	6.2			
167.2	0.446	0.250	28.4	68.5	3.1	7.9	86.0	6.1	1.096	0.0331	0.0684
	0.449	0.246	28.4	68.3	3.3	7.8	86.4	5.8			
249.3	0.393	0.303	21.6	74.7	3.7	12.3	82.2	5.5	2.41	0.0852	0.276
	0.398	0.299	21.6	74.3	4.1	11.7	81.8	6.5			
252.8	0.385	—	19.8	75.9	4.3	—	—	—	3.45	0.1364	0.555
	0.382	0.380	—	—	—	18.8	76.8	4.4			

Temperature, 85° C.

1	0.628					67.7	32.3				
34.8	0.602	0.0241	86.5	13.0	0.5	4.0	91.8	4.2	0.1503	0.0417	0.0462
	0.572	0.0735	65.1	33.9	1.0	3.1	91.1	5.8			
100.9	0.521	0.1370	48.6	49.4	2.0	5.2	88.7	6.1	1.016	0.0549	0.107
	0.389	0.264	—	—	—	12.7	81.9	5.4			
167.2	0.395	0.262	26.4	69.5	4.1	13.0	82.1	4.9	2.63	0.1473	0.486
	0.363	0.342	22.8	73.5	3.7	20.7	75.2	4.1			
242.5	0.343	0.341	20.1	76.3	3.6	19.9	76.2	3.9	3.79	0.248	0.99
	0.343	0.341	—	—	—	—	—	—			

Fig. 3, show a marked concavity with a reversal in trend occurring over the pressure range 150 to 200 atm. This tendency of the composition curves to approach a maximum in respect to gas content of the liquid phase is more

marked here than it is in the pentane or hexane systems. This phenomenon, observed by Bassett and Dode (1) in the nitrogen-water system in such degree that no single phase region is exhibited, depends apparently on the mutual solubility of the components of the system.

Hill and Lacey (4) have given the composition at one point, 20.4 atm. and 30° C. for the liquid phase, as 9.6 mole per cent methane. Extrapolation

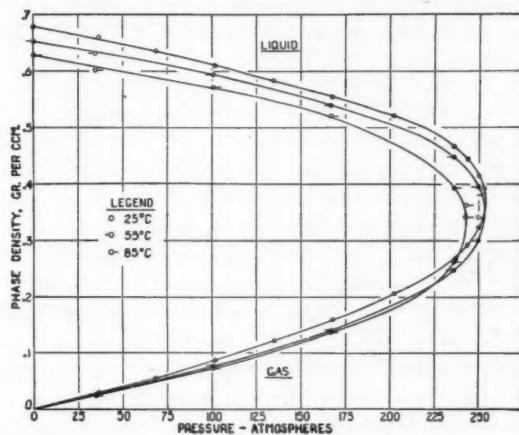


FIG. 2. Density of gas and liquid phases at constant temperatures as a function of pressure for *n*-heptane-methane (5.6% of nitrogen) system.

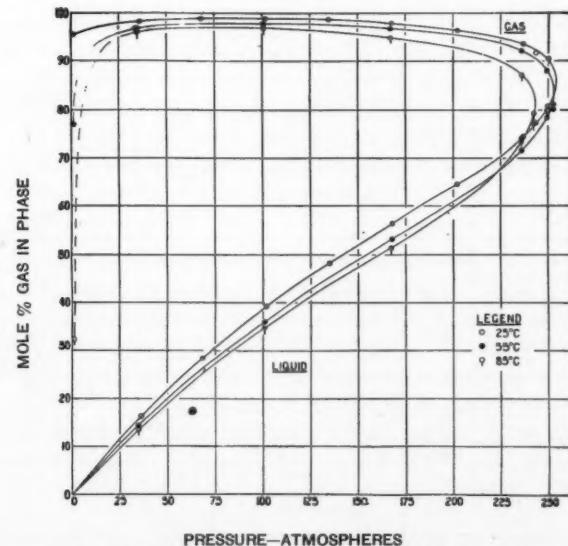


FIG. 3. Composition in mole percentage of gas and liquid phases at constant temperatures as a function of pressure for *n*-heptane-methane (5.6% of nitrogen) system.

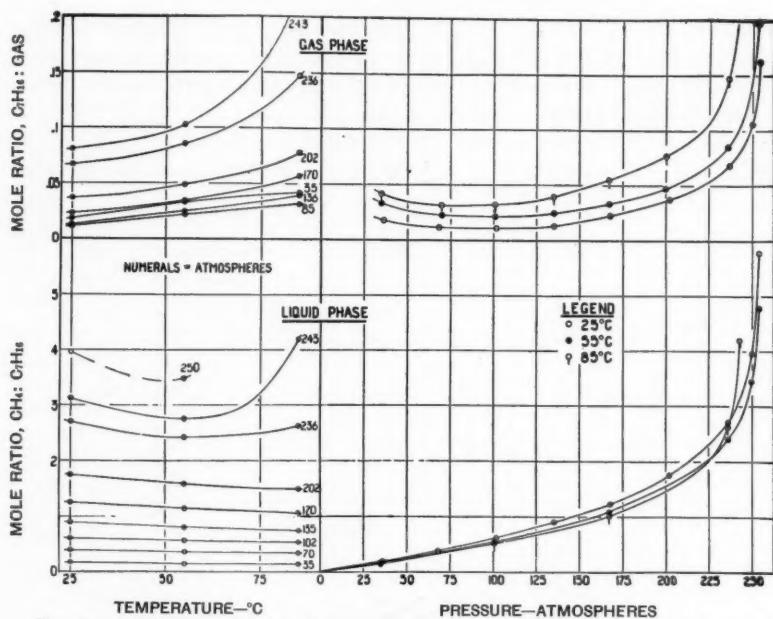


FIG. 4. Solubilities, as mole ratios of methane to *n*-heptane in liquid phase and *n*-heptane to gas in gas phase, as functions of temperature and pressure.

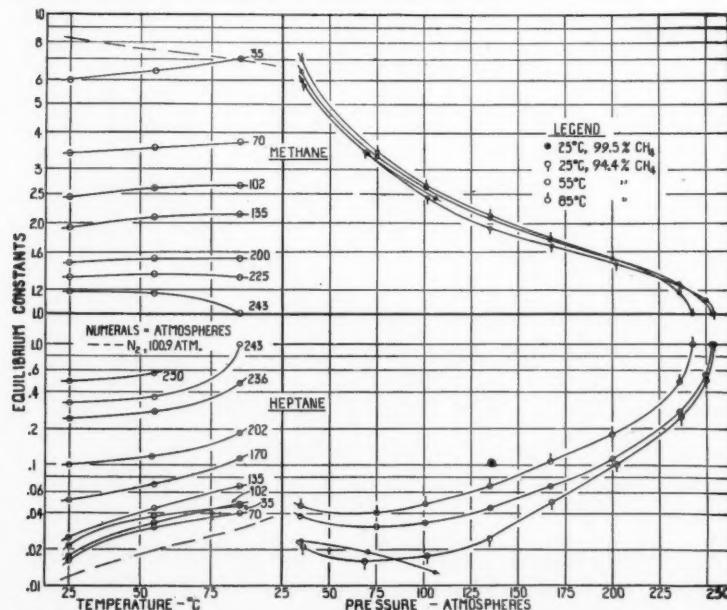


FIG. 5. Equilibrium constants, K_1 for methane and K_2 for *n*-heptane, as functions of temperature and pressure, including data on nitrogen and pure methane systems.

of the present data to 20.4 atm. and interpolation to 30° C. gives a result, 9.4%, in good agreement with that of Hill and Lacey.

It is of interest to compare the present results with those of Kay (5) on the *n*-heptane-ethane system. The great influence of the gas may be illustrated best by the difference in pressure of complete miscibility. Replacing methane by ethane results in a drop of more than half in this pressure. A consideration of the equilibrium constants in the two systems indicates that the systems behave in much the same manner with changing temperature and pressure. The magnitude of the constant for methane is, however, roughly five times that for ethane. The greater solubility of ethane compared to methane accounts for this. The constant for heptane, K_2 , is not independent of the gas. At low pressures and temperatures, the constant is smaller in the presence of ethane than it is in the presence of methane. This result can be attributed only to the influence exerted by the liquid phase on the composition of the gas phase. Although heptane should move into a gas phase composed of ethane more readily than into a gas phase composed of methane, the concentration of heptane in the liquid phase is so low that the opposite is true. Stated in another way, the more soluble ethane reduces the concentration of heptane in the liquid phase, with the result that the concentration of heptane in the gas phase is reduced, relatively, a greater amount than it is in the methane-heptane system.

At pressures greater than about 70 atm. the constant for heptane in the ethane-heptane system becomes greater than the constant in the methane-heptane system. This is, of course, to be expected since the constant approaches 1 at the pressure of complete miscibility, less than 100 atm. in the first system and more than 250 atm. in the second. It is characteristic of K_2 that at low pressures it changes only slowly, and at pressures about 75% of those at the point of miscibility it increases very rapidly. This change in trend occurs at about 70 atm. in the ethane-heptane system and at 200 atm. in the methane-heptane system. Finally, it is to be noted that both equilibrium constants in the ethane-heptane system change more rapidly with temperature than they do in the methane-heptane system.

The Influence of Nitrogen

The properties of the system, *n*-heptane-nitrogen at a pressure of 100.9 atm. and at different temperatures from 25° to 115° C. are given in Table IV. The system is shown graphically in Fig. 6, together with the comparable data from Table III on the *n*-heptane-methane (5.6% of nitrogen) system. Further, the essential data on the nitrogen system and the corresponding data on nitrogen in the *n*-heptane-methane (5.6% of nitrogen) system are given in Table V. The equilibrium constants for nitrogen are shown graphically as dotted lines in Fig. 5.

The solubility of nitrogen in *n*-heptane is approximately only one-third that of methane. Further, *n*-heptane vaporizes into methane to a greater extent than it does into nitrogen. The behavior of the methane system at 35 atm. is about the same as that of the nitrogen system at 100.9 atm. The

TABLE IV
NITROGEN-*n*-HEPTANE SOLUBILITY EQUILIBRIUM AT 100.9 ATM. PRESSURE

Temper- ature, °C.	Phase density, gm. per cc.		Phase composition, mole %				Solubility		Equilibrium constant	
			Liquid		Gas					
	Liquid	Gas	C_7H_{16}	N_2	C_7H_{16}	N_2	S_1''	S_2'	X_2'/X_1''	X_1'/X_1''
25	0.673	0.0993	88.0	12.0	1.04	98.96	0.136	0.0105	0.0118	8.24
55	0.653	0.109	87.2	12.8	1.76	98.24	0.147	0.0179	0.0202	7.54
85	0.625	0.109	86.7	13.3	1.75	98.25	0.162	0.0256	0.0289	6.99
115	0.593	0.098	85.02	14.98	5.05	94.95	0.177	0.0526	0.0594	6.34

effect of temperature changes on the two systems is very different. It may be seen in Fig. 6 that the solubility of nitrogen in *n*-heptane increases with increasing temperature, while the normal reverse behavior holds for methane under the same conditions. The solubility of methane in *n*-heptane increases

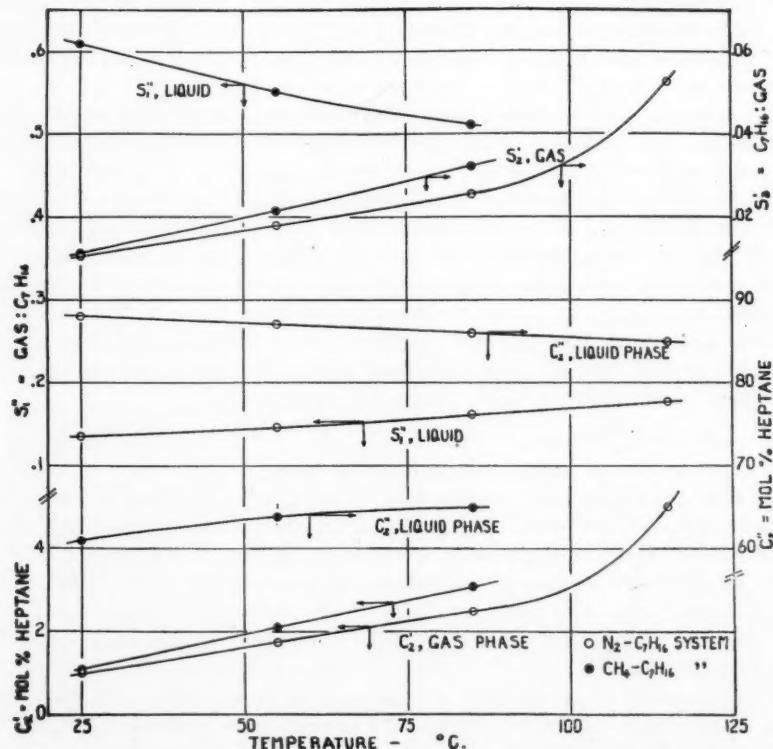


FIG. 6. The properties of the *n*-heptane-nitrogen system and the *n*-heptane-methane system (5.6% of nitrogen) system at 100.9 atm. as a function of temperature.

with increasing temperature only at pressures above 225 atm. and in the temperature range above 50° C. Presumably nitrogen would behave like methane at some pressure range below 100.9 atm. and at lower temperatures.

TABLE V
COMPARISON OF HEPTANE-METHANE (5.6% OF NITROGEN) AND HEPTANE-NITROGEN SYSTEM
AT 100.9 ATM.

Temperature, °C.	Nitrogen, mole %				Equilibrium constant, N ₂		Equilibrium constant, C ₇ H ₁₆		Solubility N ₂ in liquid		Solubility, calculated
	Liquid phase		Gas phase		1	2	1	2	1	2	
	1	2	1	2	1	2	1	2	1	2	
25	0.7	12.0	5.9	98.95	8.4	8.24	.018	.0118	.0115	.136	.0081
55	0.9	13.1	5.1	98.24	5.7	7.54	.0329	.0202	.0141	.147	.0073
85	1.0	14.0	5.8	97.5	5.8	7.0	.0476	.0289	.0154	.162	.0097

NOTE: 1—refers to heptane-methane (5.6% of nitrogen) system, Table III.

2—refers to heptane-nitrogen system, Table IV.

The distribution of nitrogen between the gas and liquid phases of the *n*-heptane-methane (5.6% of nitrogen) system as given in Table III has been used to calculate solubilities and equilibrium constants given in Table V. The results are only approximate because of the small concentrations of nitrogen involved. In addition, the solubility of nitrogen in *n*-heptane at pressures corresponding to the partial pressures of nitrogen in the *n*-heptane-methane (5.6% of nitrogen) system has been calculated from the data on the *n*-heptane-nitrogen system. Henry's law and identical liquid phases have been assumed. The calculated values are a little lower in all cases than the observed values. The discrepancy is in the right direction when it is considered that the two liquid phases are not identical. The liquid phase in the methane system is much less dense than the liquid phase in the nitrogen system, and contains much methane. Nitrogen would be more soluble in the *n*-heptane-methane mixture than in *n*-heptane alone. The error involved in the assumption of Henry's law is, probably, not significant. The data of Table V suggest the conclusion that, for practical purposes, the behavior of the nitrogen in the *n*-heptane-methane (5.6% of nitrogen) system may be determined on the basis of Henry's law. In other words, nitrogen at low partial pressures behaves ideally in the *n*-heptane-methane (5.6% of nitrogen) system.

A study of the equilibrium constants for nitrogen confirms the previous conclusion. It is roughly true that the constants for nitrogen given in Table V are much the same in the two systems. As would be expected, the constant for nitrogen is several times as great as that for methane, and, further, while the constants for methane increase with temperature, the constants for nitrogen decrease with increase in temperature. This result follows from the nature of the solubility changes with temperature.

The constants for *n*-heptane given in Table V for the two systems are different by significant amounts but change with temperature in the same manner. The constant for *n*-heptane is less in the nitrogen system than it is in the methane system. This result follows from a low concentration of *n*-heptane in the gas phase and a high concentration in the liquid phase of the nitrogen system. The low concentration of *n*-heptane in the gas phase occurs in spite of the high concentration of *n*-heptane in the liquid phase, and must be attributed to the lack of any molecular similarity between *n*-heptane and nitrogen. The statement that compressed gaseous nitrogen is a poorer solvent than methane for *n*-heptane, while unconventional, expresses the conditions fairly well. Previously, in a discussion of the relations between the *n*-heptane-methane and *n*-heptane-ethane systems, the concentration of *n*-heptane in the liquid phase was considered to control the gas phase composition. Molecular similarity is the more important variable in the comparison of the *n*-heptane-nitrogen and *n*-heptane-methane systems.

TABLE VI
METHANE (0.5% OF NITROGEN)-*n*-HEPTANE SOLUBILITY EQUILIBRIUM AT 25° C.

Pressure, atm.	Phase density, gm. per cc.	Phase composition, mole %								Solubility		Equilibrium constant	
		Liquid				Gas							
		Liquid	Gas	C ₇ H ₁₆	CH ₄	N ₂	C ₇ H ₁₆	CH ₄	N ₂	S _{1''}	S _{1'}	X _{1'} /X _{1''}	X _{1'} /X _{1''}
35	0.658	0.0275	83.8	16.2	0.0	1.95	97.33	0.72	0.1945	0.0199	0.0233	5.98	
	0.658	—	83.7	16.3	0.0	—	—	—	—	—	—		
70.4	0.634	0.0521	71.2	28.8	0.0	1.70	98.30	0.0	0.4065	0.0139	0.0193	3.42	
	0.633	0.0532	70.9	28.9	0.2	1.04	98.96	0.0	—	—	—		
106	0.605	0.0852	59.3	40.7	0.0	0.71	99.26	0.03	0.685	0.00785	0.0130	2.43	
	0.607	0.0855	59.3	40.6	0.1	0.83	98.67	0.50	—	—	—		

In order to have further information on the influence of nitrogen on the systems involving methane, the data of Table VI were obtained. The methane used in these experiments contained only 0.5% of nitrogen. The liquid phases in the two series of experiments, Tables III and VI, are identical for all practical purposes. Evidently the presence of 5.6% of nitrogen in the methane used does not change the composition of the liquid phase by any great amount. The data have not been plotted in Fig. 3 because they lie so close to the curve for 25° C. but are shown as equilibrium constants in Fig. 5. There is a small difference between the composition of the two liquid phases which is in the correct direction of higher gas content when 0.5% of nitrogen is present. The compositions of the gas phases in the two cases are not in agreement. The deviations are erratic and are due, probably, to experimental error. In conclusion, for practical purposes nitrogen in methane to the extent of 5.6% at least can be ignored as far as its influence

on the composition of the liquid phase is concerned. The behavior of the nitrogen can be predicted on the assumption that it is an ideal gas and obeys Henry's law. If desired, its presence may be corrected for by considering the pressure on the system as that measured, less the Dalton partial pressure of nitrogen, and calculating compositions on the basis of hydrocarbons only.

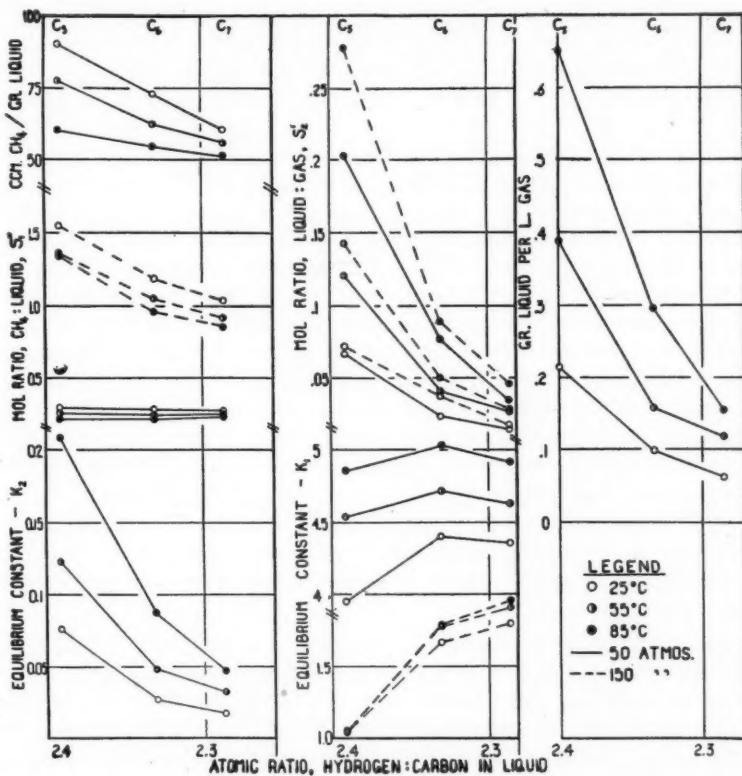


FIG. 7. Comparison of the properties of *n*-pentane-, *n*-hexane-, *n*-heptane-methane (5.6% of nitrogen) systems on the basis of hydrogen-carbon atom ratio in liquid hydrocarbon.

Comparison of the Pentane-, Hexane-, Heptane-methane Systems

Some of the data of Table III and corresponding data from previous papers (2, 3) are shown graphically in Fig. 7. The atomic ratio of hydrogen to carbon has been used as the distinguishing characteristic for the hydrocarbons and appears as abscissa. Many other properties of the molecule as, for example, molecular weight, volume, boiling point, freezing point, and refraction, were investigated, but no regularities such as straight lines were found. In Table VII are given the properties of the three systems, methane-pentane, -hexane, and -heptane at the pressure of complete miscibility.

TABLE VII
CONDITIONS AT PRESSURE OF COMPLETE MISCELLIBILITY FOR THREE SYSTEMS, METHANE-PENTANE,
-HEXANE, -HEPTANE

Carbon number	Temperature, °C.	Pressure, atm.	Density, gm. per cc.	Liquid, mole %	S_1''	S_2''
5	25	175	0.307	19	4.02	0.234
6	25	214	0.347	16.5	5.38	0.1975
7	25	254	0.370	14	5.78	0.163
5	55	171	0.293	25	2.91	0.333
6	55	210.5	0.325	19.7	4.36	0.246
7	55	253	0.350	16.5	4.79	0.198
5	85	162	0.285	31	2.75	0.450
6	85	201	0.310	23.5	3.50	0.307
7	85	243	0.330	18.5	4.20	0.227

In their general behavior, the properties of the three systems change regularly. The curvature of the liquid phase composition line, Fig. 3, is most pronounced for the heptane system and least for the pentane system. Again, in the neighborhood of the pressure of complete miscibility, the peak of the curve is sharpest for the heptane system and flattest for the pentane system. According to the gas phase composition curves, the minimum of vapor content occurs at about the same pressure, 75 to 100 atm., irrespective of compound or temperature. The vapor content of the gas phase varies with the compound, however, and is roughly proportional to the normal vapor pressure of the compound. This is illustrated by the solubility, S_2' , and number of grams of liquid per litre of gas, in Fig. 7. The effect of rising temperature on the vapor content of the gas phase is the same for all; the vapor content increases. The effect is most marked for pentane and least for heptane.

The solubility of gas in liquid, S_1'' , expressed as a mole ratio, changes only slightly with the hydrogen-carbon ratio at low pressures. At high pressures, however, as shown by the 150 atm. lines of Fig. 7, the solubility decreases with decreasing hydrogen-carbon ratio; that is, in going from pentane to heptane. This is the behavior to be expected. When solubilities are expressed as cubic centimetres of gas per gram of liquid, the solubility decreases from pentane to heptane at all pressures and nearly linearly. A rise in temperature results generally in a decrease in S_1'' and the effect is most marked with pentane. However, at high pressures or high temperatures or both, the solubility will increase with increasing temperature. In the range of temperature studied, this effect becomes observable at 150 atm. for pentane, 187 atm. for hexane, and 227 atm. for heptane. It is of interest to remember that in the nitrogen-heptane system, S_1'' increased linearly with temperature in the range studied at 100.9 atm. (Fig. 6).

The magnitude of S_1'' may be very great as the pressure of complete miscibility is approached. The highest values are shown by the heptane system. However, at equal pressures, below the pressure of miscibility for all the

systems being compared, S_1'' is always greatest for pentane and least for heptane.

The behavior of the equilibrium constants is very similar for the three systems, with a regular variation from compound to compound. At all comparable pressures, K_2 decreases in going from pentane to heptane, and changes most with temperature in the case of pentane. At the pressure of minimum K_2 , about 100 atm., the effect of temperature is most pronounced. The data of Nederbragt (6) on butane fit in well with the present work, the equilibrium constant for butane being greater than that for pentane at the same temperature and pressure.

The equilibrium constant for methane, K_1 , at pressures above 50 atm., increases in going from pentane to heptane. At low pressures and high temperatures, K_1 is, roughly, constant for all compounds and is sensitive to temperature. A maximum is shown for hexane at 50 atm. which is characteristic at low pressures. The data of Nederbragt (6) for methane in the methane-butane system fit these results. K_1 in the methane-butane system is less than K_1 in the methane-pentane system at the same temperature and pressure.

The change in the equilibrium constant for methane, K_1 , with the liquid component is not very great under any conditions, but is real. Only if the systems were ideal, would a constant K_1 , independent of the liquid component, be found. It might be predicted that K_1 will approach a constant limiting value for paraffin hydrocarbons higher than those used here. The change in equilibrium constant for the liquid, K_2 , with change in the liquid component, is relatively very great at the higher hydrogen-carbon ratio and higher temperatures. However, there is a suggestion that with the higher paraffin hydrocarbons, K_2 changes only slightly and may approach a minimum limiting value.

In Table VII, describing the systems at the pressure of complete miscibility, the change shown in properties with change in liquid component is just what might be expected. The change in the pressures is very regular. Upon increase of the carbon number by one, the pressure of complete miscibility increases by .40.5 atm. with a maximum deviation of 2 atm. in this series at all three temperatures used. Interpolation of the results obtained by Sage, Lacey and Schaafsma (7) with the propane-methane system gives a value of 39 atm. per carbon atom difference between propane and pentane at 25° C. The rule does not hold at higher temperatures, the figures being 44.5 and 52.5 atm. at 55° and 85° C.

The region of retrograde condensation, that is, the region between the pressure of complete miscibility and the point of minimum vapor content of the gas phase, is largest for heptane and least for pentane. This region in the methane-propane system (7) is still more restricted than in the pentane system. Further, as might be predicted, the region of retrograde condensation is reduced by rising temperature.

The changes in the other properties, such as density and composition, (Table VII) with the compounds are in the direction expected. Generally, the shift, such as the increase in density or decrease in liquid content of the system, is greater in the interval, pentane-hexane, than in the interval, hexane-heptane. There is a very great change in composition of about 100% increase in liquid content in going from the pentane system to the propane system (7).

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THE KINETICS OF THE DECOMPOSITION REACTIONS OF THE LOWER PARAFFINS

III. PROPANE¹

By E. W. R. STEACIE² AND I. E. PUDDINGTON³

Abstract

The kinetics of the thermal decomposition of propane has been investigated over a temperature range from 551° to 602° C. The limiting high pressure first order rate constants are given by

$$\log_{10} k = 13.46 - \frac{63300}{2.3RT} \text{ sec.}^{-1}$$

The first order rate constants fall off strongly with increasing percentage decomposition, and the rate decreases with decreasing pressure in a manner similar to the rate decrease in the decomposition of the butanes.

Analyses of the products of reaction at various stages show them to be independent of temperature over the range examined, but to be affected by the initial pressure. This effect is undoubtedly due to the secondary hydrogenation of some of the initial products. The analytical results are in excellent agreement with those of Frey and Hepp.

Introduction

Recent papers from this laboratory (15, 16, 17) have pointed out the need for further work on the kinetics of the thermal decomposition reactions of the simple paraffin hydrocarbons. Investigations of the kinetics of the decomposition of *n*-butane (16) and isobutane (17) have already been reported. The present paper deals with propane.

Early work with propane (4, 7, 11, 12, 13) showed the decomposition to be fundamentally homogeneous and first order, the main reactions being



Ethane and butane have also been reported as primary products, but in relatively small amounts.

Marek and McCluer (8), using a flow method, found the products to be as indicated by the above equations, in approximately equal amounts. They reported that the rate, after correction for the back reactions, is given by

$$\log_{10} k = 13.44 - \frac{62100}{2.3RT} \text{ sec.}^{-1}$$

Later Paul and Marek (10) examined the reaction more thoroughly, using low conversions to eliminate secondary processes. Change of the surface and of the surface/volume ratio were found to be without effect on the rate. The temperature coefficient was found to differ greatly from that indicated by the previous equation, being given by

$$\log_{10} k = 16.60 - \frac{74850}{2.3RT} \text{ sec.}^{-1}$$

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Frey and Hepp (6) investigated the reaction at one temperature only, using a flow system. Their absolute rates were in good agreement with those obtained by other workers. Thorough analyses of the products of the reaction were made by low temperature distillation. These will be discussed later.

Dintzes and Frost (1, 2, 3) examined the reaction at temperatures from 619° to 666° C., and at initial pressures from 1 to 78 mm., using a static system. They found that the unimolecular constants fell off very strongly during an individual run. The addition of hydrogen, methane, or ethylene had no apparent effect on the reaction rate.

In view of the widely different values reported for the activation energy of the reaction, re-investigation with particular attention to the temperature coefficient seemed to be desirable.

Experimental

A static method, which has been previously described (16), was used. The products of the reaction were analyzed by low temperature fractional distillation in a still of the Podbielniak type. In the analyses considerable difficulty was experienced in obtaining a sharp cut between propane and propylene. To obviate this difficulty propane and propylene were taken off as a single fraction, and the propylene in this fraction was determined by absorption in fuming sulphuric acid in a Burrell gas analysis apparatus. Analyses were made on samples withdrawn from the reaction system at 6, 12.5, 25, and 50% pressure increase.

Propane of 99.9% purity was obtained in cylinders from the Ohio Chemical and Mfg. Co., and was used without further purification.

Results

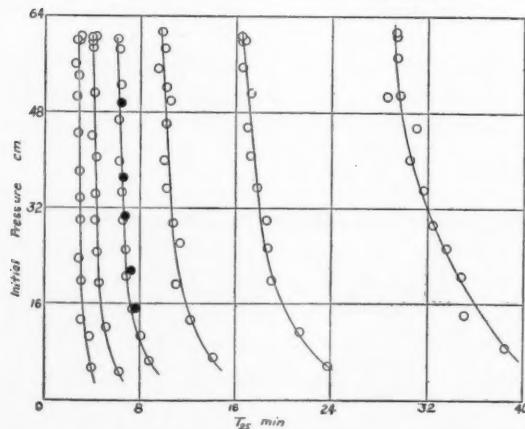


FIG. 1. Effect of pressure and temperature on the reaction rate. The curves from left to right represent respectively 602°, 592°, 582°, 572°, 562°, 551°, C. Black circles are the results of experiments in a packed reaction vessel.

The Rate of the Reaction

The reaction rate was followed by observing the pressure increase in a system of constant volume, as before. The results of rate experiments are given in Table I, in which $T_{12.5}$ and T_{25} correspond to the times for a 12.5 and a 25% pressure increase, respectively. The data are shown graphically in Fig. 1.

Limiting high pressure rates were found in the usual way by plotting T_2

TABLE I
THE EFFECT OF TEMPERATURE AND PRESSURE ON THE REACTION RATE

Initial pressure, cm.	$T_{12.5}$, min.	T_{25} , min.	Initial pressure, cm.	$T_{12.5}$, min.	T_{25} , min.
<i>Temperature, 602° C.</i>					
60.5	0.9	2.7	33.8	1.0	3.0
59.5	1.0	2.9	30.0	1.0	3.0
56.0	0.8	2.5	23.8	1.0	2.9
54.0	0.9	2.8	19.8	1.0	3.1
50.5	0.9	2.7	13.5	1.0	3.1
44.2	0.9	2.8	10.5	1.3	3.8
38.0	1.0	3.0	5.25	1.5	4.0
<i>Temperature, 592° C.</i>					
60.6	1.4	4.2	40.2	1.4	4.3
60.1	1.4	4.0	34.5	1.5	4.3
59.8	1.4	4.0	30.0	1.5	4.3
59.5	1.3	4.0	24.5	1.5	4.4
58.5	1.4	4.0	19.5	1.5	4.6
51.3	1.4	4.1	12.10	1.6	5.2
44.3	1.3	3.9	4.40	2.0	6.3
<i>Temperature, 582° C.</i>					
60.0	2.1	6.1	30.10	2.2	6.6
58.5	2.0	6.2	25.10	2.3	6.9
52.4	2.2	6.4	20.30	2.3	6.9
46.5	2.1	6.2	15.50	2.4	7.4
39.80	2.1	6.3	10.95	2.9	8.1
34.65	2.2	6.5	6.45	3.0	8.8
<i>Temperature, 582° C. Packed reaction vessel</i>					
48.8	—	6.4	21.1	2.4	7.3
36.4	2.2	6.5	15.0	2.5	7.6
30.8	—	6.8			
<i>Temperature, 572° C.</i>					
61.7	3.5	9.8	35.1	3.4	10.3
58.3	3.4	10.0	29.7	3.5	10.8
55.4	3.2	9.5	25.95	3.9	11.4
51.9	3.5	10.2	19.50	3.7	11.1
49.8	3.6	10.5	13.42	4.2	12.3
46.5	3.4	10.1	6.76	5.0	14.1
39.9	3.3	10.0			
<i>Temperature, 562° C.</i>					
60.45	5.8	16.5	35.10	6.1	17.8
60.00	5.8	16.8	30.00	6.3	18.5
59.90	5.6	16.5	25.30	6.2	18.4
55.45	5.7	16.5	19.90	6.2	19.0
50.65	5.6	17.2	11.25	7.0	21.4
45.30	5.9	17.0	5.87	7.5	23.8
40.70	—	17.3			

TABLE I—Concluded

THE EFFECT OF TEMPERATURE AND PRESSURE ON THE REACTION RATE—Concluded

Initial pressure, cm.	$T_{12.5}$, min.	T_{25} , min.	Initial pressure, cm.	$T_{12.5}$, min.	T_{25} , min.
<i>Temperature, 551° C.</i>					
57.15	10.1	29.4	29.20	11.2	32.4
51.00	10.3	29.6	25.40	11.4	33.6
50.65	9.8	28.6	20.23	11.4	34.8
45.30	10.8	31.0	14.15	11.6	35.1
40.35	10.8	30.5	8.72	12.2	38.5
34.80	10.8	31.7			

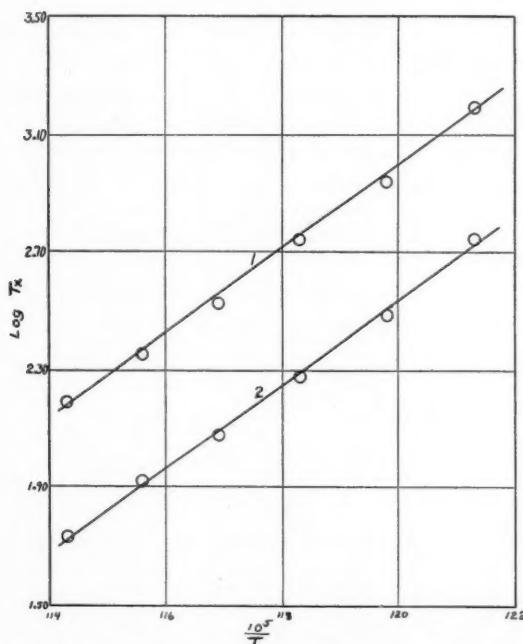


FIG. 2. The effect of temperature on the rate of the reaction.

against the reciprocal of the initial pressure, and extrapolating to infinite pressure. The values thus obtained are given in Table II.

The temperature coefficient of the reaction is shown graphically in Fig. 2, in which Curve 1 represents the values of T_{25} , and Curve 2 those of $T_{12.5}$. These curves lead to values of the activation energy of 63,600 and 62,900 cal. per mole, respectively. Since the ratio $T_{25}/T_{12.5}$ is independent of the temperature, and of the initial pressure, it is justifiable to infer the activation

TABLE II
LIMITING HIGH PRESSURE RATES

Temperature, °C.	$T_{12.5}$, min.	T_{25} , min.	$\frac{T_{25}}{T_{12.5}}$	Limiting high pressure rate constant, sec. ⁻¹ (calculated from T_{25})
602	0.91	2.60	2.86	18.5×10^{-4}
592	1.35	3.75	2.78	12.8×10^{-4}
582	2.00	5.55	2.78	8.65×10^{-4}
572	3.16	9.15	2.89	5.24×10^{-4}
562	5.10	14.50	2.85	3.31×10^{-4}
551	9.30	26.00	2.80	1.84×10^{-4}

energy from values of T_{25} or $T_{12.5}$. The high pressure rate constants calculated from values of T_{25} are also given in Table II. From these values we obtain for the high pressure rate at any temperature (as calculated from T_{25})

$$\log_{10}k = 13.16 - \frac{63300}{2.3RT} \text{ sec.}^{-1}$$

Table III gives complete data for two typical runs at 582° C. The falling off in the rate constants as the reaction progresses is noteworthy. Similar behavior has been found by Dintzes and his collaborators (1, 2, 3). The rate

TABLE III
COMPLETE DATA FOR TYPICAL RUNS

Initial pressure, 39.80 cm. Temperature, °C., 582			Initial pressure, 46.5 cm. Temperature, °C., 582		
Time, min.	ΔP , cm.	k , sec. ⁻¹	Time, min.	ΔP , cm.	k , sec. ⁻¹
0.0	—	—	0.0	—	—
0.5	1.75	15.3×10^{-4}	0.5	2.1	15.4×10^{-4}
1.0	2.80	12.3	1.0	3.4	12.6
1.5	3.90	11.5	1.5	4.6	11.8
2.0	4.95	11.1	2.0	5.8	11.3
3.0	6.20	9.48	3.0	7.3	9.44
4.0	7.48	8.74	4.0	8.8	8.70
5.0	8.58	8.05	5.0	10.2	8.20
6.0	9.59	7.67	6.0	11.4	7.80
6.3	9.95	7.63	6.2	11.6	7.73

constants in Table III are calculated on the assumption that 100% pressure increase corresponds to completion. Analytical results given later show that up to 25% decomposition the pressure change is an accurate measure of the percentage decomposition, and hence justify the method of calculating the rate constants. At higher percentage decompositions, however, considerable polymerization, hydrogenation, and other secondary reactions occur, and the pressure increase is therefore a somewhat unreliable measure of the extent of reaction. It appears from Table III, and from similar calculations for other runs, that the initial rate constants are approximately 100% higher than those

at 25% decomposition. We may therefore correct the above equation, and obtain for the initial high pressure rate constants

$$\log_{10}k = 13.46 - \frac{63300}{2.3RT} \text{ sec.}^{-1}$$

In Fig. 1 the filled circles represent runs made in a reaction vessel filled with broken quartz, so as to increase the surface/volume ratio by a factor of about 15. It is evident that no appreciable increase in rate occurs with increased surface, and hence the reaction is completely homogeneous.

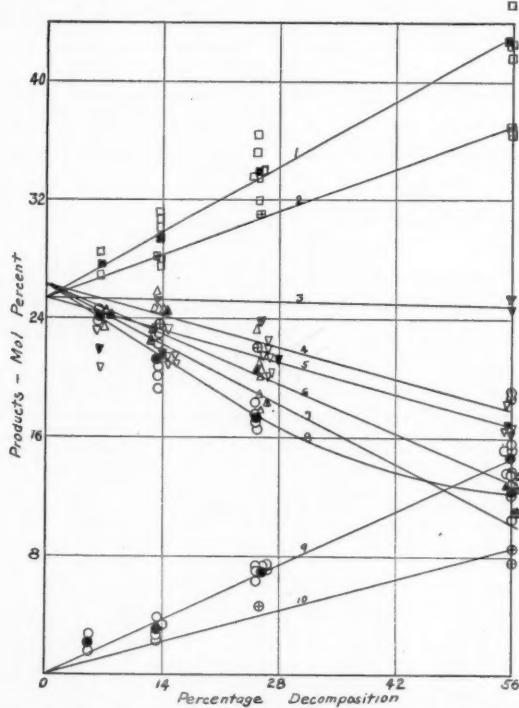


FIG. 3. Extrapolation to determine initial products of the reaction. Open symbols represent actual analyses; black symbols represent mean values. From top to bottom the curves represent successively CH_4 , CH_4 at low pressure, C_2H_4 at low pressure, H_2 at low pressure, C_2H_4 , C_3H_6 , C_3H_6 at low pressure, H_2 , C_2H_6 , and C_2H_6 at low pressure.

The Products of the Reaction

Analyses of the products of the reaction were made over the temperature range from 551° to 602° C., and at initial pressures of 60 and 20 cm. Products were withdrawn for analysis at times corresponding to pressure increases of 6, 12.5, 25, and 50%. The results of these analyses are given in Table IV, and are shown graphically in Fig. 3.

TABLE IV
THE PRODUCTS OF THE REACTION

Products, mole per cent	Temperature, °C.						
	551	562	572	582	592	602	Mean
<i>Initial pressure, 60 cm. Sample withdrawn at T_{50}</i>							
H_2	—	—	10.6	12.3	13.3	13.5	12.4
CH_4	—	—	44.8	42.6	42.5	41.5	42.8
C_2H_4	—	—	16.1	16.2	18.5	16.7	16.9
C_2H_6	—	—	15.8	15.4	12.8	15.3	14.8
C_3H_6	—	—	12.4	13.5	12.8	13.0	12.9
% Decomposition	—	—	58.6	55.0	57.3	52.6	56.1
<i>Initial pressure, 60 cm. Sample withdrawn at T_{25}</i>							
H_2	17.0	17.4	16.6	17.2	18.5	15.5	17.0
CH_4	36.5	33.9	33.6	31.8	33.5	35.3	34.1
C_2H_4	22.0	22.4	21.6	20.3	20.2	21.5	21.3
C_2H_6	6.5	7.4	7.1	7.3	7.2	7.4	7.1
C_3H_6	18.0	19.0	21.1	23.4	20.5	20.2	20.8
% Decomposition	24.4	25.0	25.4	26.2	25.0	24.6	25.1
<i>Initial pressure, 60 cm. Sample withdrawn at $T_{12.5}$</i>							
H_2	20.2	19.4	20.8	23.0	22.5	—	21.2
CH_4	30.6	31.1	29.8	28.0	27.6	—	29.4
C_2H_4	21.5	23.5	20.8	21.0	21.3	—	21.6
C_2H_6	3.1	2.4	2.6	3.2	3.9	—	3.1
C_3H_6	24.7	23.5	25.9	24.8	24.7	—	24.7
% Decomposition	12.6	12.8	12.4	14.2	14.2	—	13.6
<i>Initial pressure, 60 cm. Sample withdrawn at T_6</i>							
H_2	24.3	24.2	—	—	—	—	24.2
CH_4	27.0	28.4	—	—	—	—	27.7
C_2H_4	23.4	20.8	—	—	—	—	22.1
C_2H_6	1.8	2.8	—	—	—	—	2.3
C_3H_6	23.4	24.5	—	—	—	—	23.9
% Decomposition	6.0	6.1	—	—	—	—	6.05
<i>Initial pressure, 20 cm.</i>							
Temperature	582		592		592		592
Sampled at	T_{50}		T_{50}		T_{25}		$T_{12.5}$
H_2	18.7		18.8		22.1		23.6
CH_4	37.0		36.6		31.0		28.3
C_2H_4	25.5		25.0		23.8		25.4
C_2H_6	7.7		8.5		4.8		0.0
C_3H_6	11.1		11.2		18.4		22.6
% Decomposition	54.0		52.8		25.5		13.1

The products are not appreciably affected by the temperature over the range examined, but vary considerably with the initial pressure, especially at high percentage decompositions. This difference appears to be due entirely to the hydrogenation of ethylene, since in both cases extrapolation to zero decomposition leads to a convergence of the curves for ethylene, ethane, and hydrogen. Ethane therefore appears to be definitely not an important initial product of the reaction.

In addition to the products listed in Table IV, a small amount of some polymer was also formed, and a visible deposit of carbon appeared on the quartz surface after a few runs. A very small amount of some higher boiling product was also observable in the still after all the gaseous products had been taken off in analyses at 50% decomposition. The amounts of carbon and polymers formed per run were, however, so small that they introduce no appreciable error into the analyses.

The Rate of the Reaction

A comparison of the initial high pressure rates obtained in this work with the rates reported by others is given in Table V.

TABLE V
COMPARISON OF RESULTS

Observers	<i>E</i> , Kcal.	$\log_{10}A$	k_{575} , sec. ⁻¹
Pease and Durgan (12)	(65.0)	—	—
Frey and Hepp (6)	—	—	—
Marek and McCluer (8)	62.1	13.44	1.5×10^{-3}
Paul and Marek (10)	74.9	16.60	2.6×10^{-3}
This investigation	63.3	13.46	1.9×10^{-3}

The absolute rates are thus in comparatively good agreement. There seems to be no doubt, however, that the values of *E* and *A* reported by Paul and Marek are very much too high.

As the products of the reaction have been shown to be independent of temperature over the range investigated, the energies of activation of the two main reactions



are identical, and equal to 63.3 Kcal. Also, as discussed in the next section, the two reactions appear to occur to the same extent in the initial stages of the decomposition. We can therefore apportion the rate constants equally between them, and we have for the separate reactions

$$\log_{10}k_1 = \log_{10}k_2 = 13.16 - \frac{63300}{2.3RT} \text{ sec.}^{-1}$$

The Products of the Reaction

As may be seen from Fig. 3, the initial products of the reaction appear to be those indicated by the above equations, in equal amount, *i.e.* 25% each of propylene, ethylene, methane, and hydrogen. This is in accord with the findings of Marek and McCluer.

As the products change greatly as the reaction proceeds, it is of course necessary to make comparisons at the same percentage decomposition, and roughly at the same pressure. Frey and Hepp reported the products at 739 mm. and 10% decomposition at 575° C. to be: H₂, 23.0; CH₄, 26.1; C₂H₄, 22.7; C₂H₆, 2.7; C₃H₆, 25.3%. Under similar conditions, the results from this investigation are H₂, 22.4; CH₄, 28.0; C₂H₄, 23.2; C₂H₆, 2.8; C₃H₆, 23.6%. The agreement is excellent.

The products are in only fair agreement with those predicted by the Rice free radical mechanism. On this basis the ratio $\frac{C_2H_4 + CH_4}{C_3H_6 + H_2}$ should have a

value of 1.5, whereas in fact it is 1.0. In any case, the work of Patat (9) has definitely shown that in its present form the Rice-Herzfeld mechanism is untenable for propane.

The Effect of Pressure on the Reaction Rate

It will be seen from Fig. 1 that the rate of reaction falls off rapidly with diminishing pressure, and that this effect is noticeable at quite high pressures. This behavior is similar to that of the butanes. As with the butanes, in order to fit the results to the Kassel theory it is necessary to consider part of the molecule to be frozen, and to reduce the number of oscillators, *s*, from the theoretical value of 19 to 7. With *s* = 7, the theory fits the results excellently if we assign to the other parameters the values *v* = 1000 cm.⁻¹, *m* = 22, σ = 4×10^{-8} cm.

In the case of the butanes, the rapid falling off in rate for such complex molecules was tentatively assumed to be due to some sort of chain process initiated by radicals. With propane, the work of Patat rules out the Rice-Herzfeld mechanism, but does not exclude the possibility of a radical chain mechanism, provided that the chains are very short. Actually, the work of Echols and Pease (5), and of Sickman and Rice (14), shows that very short chains can be initiated by the introduction of radicals into propane. Hence the effect of pressure on the rate has perhaps the same explanation for propane as for the butanes.

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